

# ELECTROCHEMICAL MEASUREMENT OF THE CHEMICAL DIFFUSION COEFFICIENT OF COPPER IN CUPROUS SULFIDE AT 400°C

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$$c_{cu}(x,t) = c''_{cu} - [c''_{cu} - c'_{cu}] \sum_{n=1,3,5}^{\infty} \frac{4}{n\pi} \sin\left(\frac{n\pi x}{l}\right) \exp\left(-\frac{n^2 \pi^2 \tilde{D}_{cu} t}{l^2}\right) \dots (3.9)$$

on differentiating with respect to  $x$ ,

$$\frac{\partial c_{cu}}{\partial x} = - (c''_{cu} - c'_{cu}) \sum_{n=1,3,5}^{\infty} \frac{4}{n\pi} \cos\left(\frac{n\pi x}{l}\right) \exp\left(-\frac{n^2 \pi^2 \tilde{D}_{cu} t}{l^2}\right) \dots (3.10)$$

$$\left(\frac{\partial c_{cu}}{\partial x}\right)_{x=0} = - (c''_{cu} - c'_{cu}) \sum_{n=1,3,5}^{\infty} \frac{4}{n\pi} \exp\left(-\frac{n^2 \pi^2 \tilde{D}_{cu} t}{l^2}\right) \dots (3.11)$$

From Fick's first law, the flux  $J$  at the  $CuBr/Cu_2S$

interface is given by

$$J = - \tilde{D}_{cu} \left(\frac{\partial c_{cu}}{\partial x}\right)_{x=0} \dots (3.12)$$

The current  $I$  is given by

$$I = JZFA.$$

where  $Z$ , refers to the oxidation state of copper ions

(univalent)  $F$  is the Faraday constant and  $A$  is the cross

sectional area of the cuprous sulfide specimen. Since  $Z = 1$ .

in the present case,

$$I = JFA \dots (3.13)$$

Using (3.13) in (3.12) we have

$$I = - \tilde{D}_{cu} FA \left(\frac{\partial c_{cu}}{\partial x}\right)_{x=0} \dots (3.14)$$

Now, from (3.11)

$$= \frac{4FA \tilde{D}_{cu}}{l} (c''_{cu} - c'_{cu}) \sum_{n=1,3,5}^{\infty} \exp\left(-\frac{n^2 \pi^2 \tilde{D}_{cu} t}{l^2}\right) \dots (3.15)$$

# **ELECTROCHEMICAL MEASUREMENT OF THE CHEMICAL DIFFUSION COEFFICIENT OF COPPER IN CUPROUS SULFIDE AT 400°C**

**A Thesis Submitted  
in Partial Fulfilment of the Requirements  
for the Degree of  
MASTER OF TECHNOLOGY**

**By  
P. D. JOSE**

**to the**

**DEPARTMENT OF METALLURGICAL ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY KANPUR  
AUGUST, 1976**

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maintained at  $(400 \pm 1^\circ\text{C})$  with the help of a Leeds and Northrup 'Electromax' controller. The temperature was measured by using a Pt-Pt 10% Rh thermocouple kept in the constant temperature zone  $(\pm 1^\circ\text{C})$  where the cell was placed.

#### 4.3 Regulated power supply

The regulated power supply fabricated in the laboratory possesses the following features:

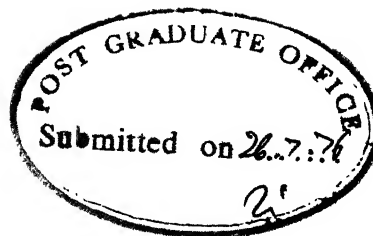
Maximum output voltage : 2250 mV.

Maximum output current : 225 mA.

Regulation : 0.6%

The regulated power supply requires  $\pm 15$  volts dc input supply. An 'Aplab' d.c. source was used for this purpose. The set-up provided a stable voltage independent of the current flowing through the cell. The current through the cell was made to pass through a known resistance (stable metal film resistors) and the voltage drop across it was then fed to a 'Sargent' strip chart recorder. The electronic circuit in the regulated power supply was so designed that the cell current was not influenced by the external resistance. This is very important since the cell resistance is very low. The circuit used is shown in Fig. 4. Desired voltages are

C E R T I F I C A T E



Certified that this work on 'Electrochemical Measurement of the Chemical Diffusion Coefficient of Copper in Cuprous Sulfide at 400°C' has been carried out under my supervision and that it has not been submitted elsewhere for a degree.

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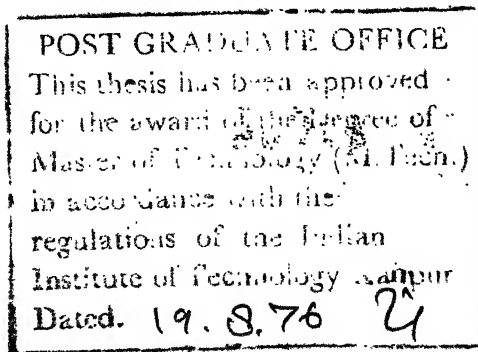


Table 3

Variation of current with time

Length of  $\text{Cu}_2\text{S}$  electrode = 2.0 cm;

Length of CuBr = 0.16 cm

$E_1 = 70 \text{ mV}$ ;  $E_2 = 90 \text{ mV}$ ;  $D = 4.513 \times 10^{-3}$

Time (sec.)	Amps. $\times 10^{-3}$	$\log I$
0	1.9029	-2.7205
62	1.4175	-2.8485
124	1.1651	-2.9337
186	0.9709	-2.0128
248	0.8156	-3.0885
310	0.6796	-3.1677
372	0.5825	-3.2347
434	0.4855	-3.3139
496	0.4175	-3.3794
558	0.3495	-3.4566

### ACKNOWLEDGEMENT

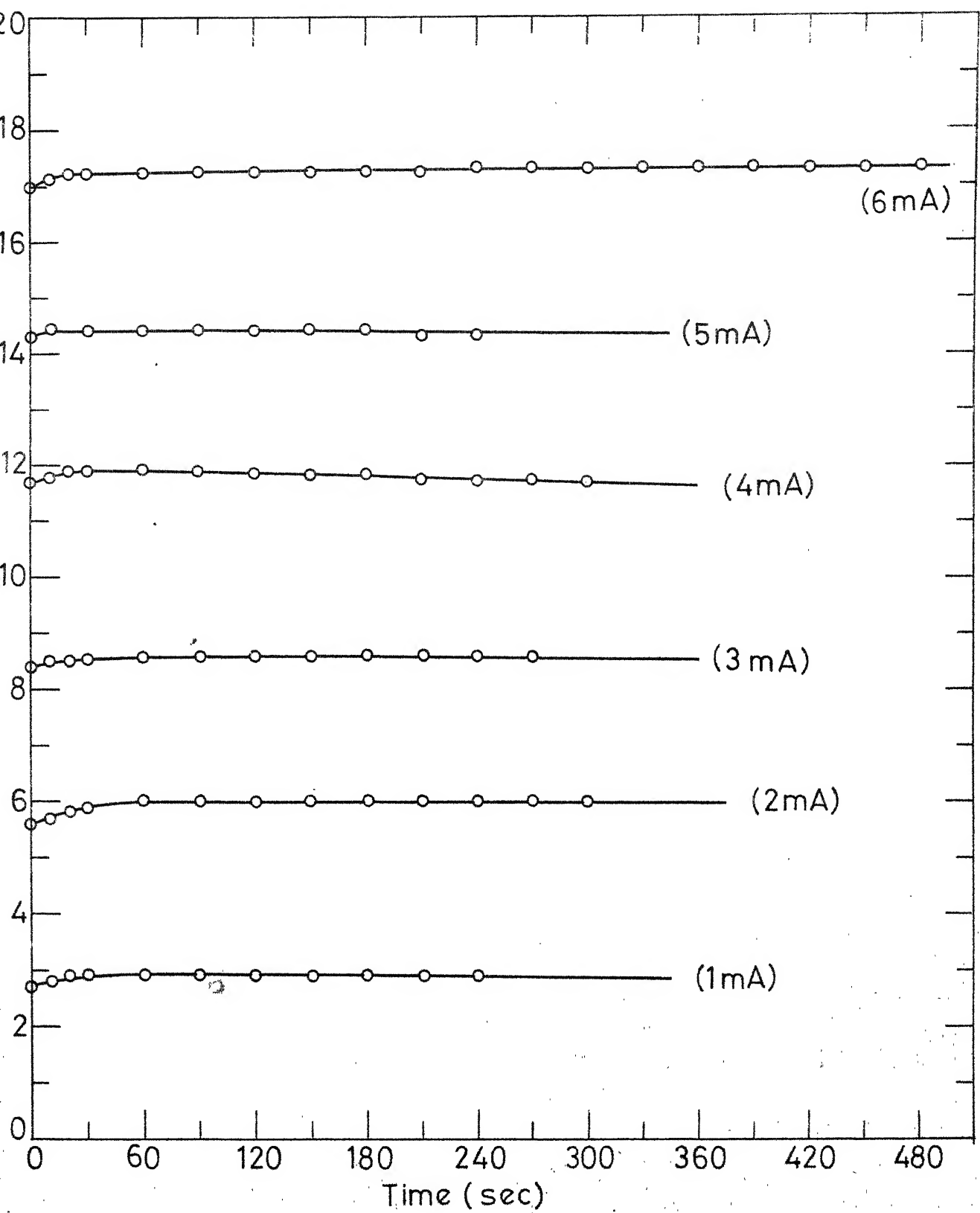
I wish to express my deep sense of gratitude to my thesis supervisor Dr. T.A. Ramanarayanan for his personal inspiration and many hours of fruitful discussions and guidance throughout the preparations of this work.

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P.D. Jose





Cathodic voltage as a function of time in the polarization experiments

FIG.11

ABSTRACT

The chemical diffusivity of copper in chalcocite was determined electrochemically as a function of the copper activity at 400°C. Potentiostatic single and double cell techniques were used in the measurements. The measured diffusivity increased with increase in the ratio of the chalcocite/electrolyte thickness and reached a constant value when the ratio was 12.5. At lower ratios, the internal resistance of the electrolyte interferes with the diffusivity measurements. The diffusivity changes from a value of  $7.22 \times 10^{-3} \text{ cm}^2/\text{Sec}$  when the copper activity is 0.7782 to a value of  $4.11 \times 10^{-3} \text{ cm}^2/\text{sec.}$  when the copper activity is 0.2311

Table 1.7

$E_1 = 40 \text{ mV}; E_2 = 70 \text{ mV};$   
 $D_{\text{Cu}} = 1.535 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. x $10^{-3}$	log I
0	3.220	-2.492
62	1.620	-2.790
124	0.020	-2.991
186	0.740	-3.130
248	0.540	-3.267
310	0.420	-3.376
372	0.300	-3.522
434	0.240	-3.619
496	0.200	-3.699
558	0.140	-3.853
620	0.120	-3.920
682	0.100	-4.000

Table 1.8

$E_1 = 70 \text{ mV}; E_2 = 100 \text{ mV};$   
 $D_{\text{Cu}} = 1.433 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. x $10^{-3}$	log I
0	3.480	-2.458
62	1.960	-2.707
124	1.320	-2.879
186	1.000	-3.000
248	0.760	-3.119
310	0.600	-3.221
372	0.440	-3.356
434	0.400	-3.397
496	0.320	-3.494
558	0.280	-3.552
620	0.240	-3.619
682	0.200	-3.699

Table 3.5

$E_1 = 30 \text{ mV}; E_2 = 10 \text{ mV};$   
 $D_{\text{Cu}} = 4.808 \times 10^{-3} \text{ cm}^2/\text{sec}.$

Time (sec.)	Amps. x $10^{-3}$	log I
0	3.100	-2.508
62	1.620	-2.790
124	1.180	-2.928
186	0.900	-3.045
248	0.700	-3.154
310	0.580	-3.236
372	0.500	-3.301
434	0.420	-3.376
496	0.380	-3.420
558	0.340	-3.468
620	0.300	-3.522
682	0.260	-3.585

Table 3.6

$E_1 = 50 \text{ mV}; E_2 = 30 \text{ mV};$   
 $D_{\text{Cu}} = 4.007 \times 10^{-3} \text{ cm}^2/\text{sec}.$

Time (sec.)	Amps. x $10^{-3}$	log I
0	3.200	-2.494
62	1.80	-2.744
124	1.400	-2.853
186	1.120	-2.950
248	0.920	-3.036
310	0.760	-3.110
372	0.640	-3.193
434	0.560	-3.251
496	0.520	-3.284
558	0.460	-3.337

CONTENTS

	Page
1. INTRODUCTION	1
2. LITERATURE SURVEY	3
2.1 Cu-S phase diagram	3
2.2 Electrical properties of chalcocite	4
2.3 Chemical Diffusion in nonstoichiometric compounds	6
3. THEORETICAL CONSIDERATIONS	11
3.1 Potentiostatic method using a single cell	11
3.2 Double cell method	14
3.3 Coulometric titration	16
4. EXPERIMENTAL MATERIALS AND PROCEDURE	19
4.1 Materials	19
4.2 Furnace	19
4.3 Regulated Power Supply	20
4.4 Cell Assembly	21
4.5a Potentiostatic single cell technique	22
4.5b Potentiostatic double cell technique	23
4.6 Coulometric titration	24
5. RESULTS AND DISCUSSIONS	25
5.1 Results	25
5.2 Discussions	29
5.3 Polarization studies	32
6. SUMMARY AND CONCLUSION	36
References	37
Appendix	40

### List of figures

Fig.	Page
1. Phase diagram of Cu-S system	3
2. Circuit for the potentiostatic single cell technique and circuit for the potentiostatic double cell technique.	14
3 a. Experimental set up	19
3 b. Cell holder	19
4. Detailed electrical circuit of the regulated power supply	20
5. Cell current versus time in the potentiostatic single cell technique	25
6. Log I versus time in the potentiostatic single cell technique	25
7. Chemical diffusion coefficient versus activity of Copper in Cuprous Sulfide at 400°C	28
8. Electrode length/electrolyte length Vs. $\bar{D}_{Cu}$	28
9. E versus $\delta$ plot	31
10. Anodic voltage as a function of time in the polarization experiments	33
11. Cathodic voltage as a function of time in the polarization experiments	33

Table 5.5

$$E_1 = 50 \text{ mv}; E_2 = 60 \text{mv};$$

$$D_{\text{Cu}} = 6.068 \times 10^{-3} \text{ cm}^2/\text{Sec.}$$

Time (Sec.)	Amps x $10^{-3}$	log I
0	0.961	-3.017
62	0.645	-3.189
124	0.504	-3.296
186	9.398	-3.400
248	0.320	-3.494
372	0.208	-3.680
434	0.169	-3.769
496	0.136	-3.866
558	0.111	-3.952
620	0.087	-4.058

Table 5.6

$$E_1 = 60 \text{mV}; E_2 = 70 \text{mV},$$

$$D_{\text{Cu}} = 5.565 \times 10^{-3} \text{ cm}^2/\text{Sec.}$$

Time (Sec.)	Amps x $10^{-3}$	log I
0	0.990	-3.004
62	0.708	-3.149
124	0.568	-3.245
186	0.461	-3.336
248	0.378	-3.421
310	0.310	-3.507
372	0.252	-3.597
434	0.208	-3.680
496	0.174	-3.757
558	0.145	-3.836
620	0.121	-3.915
682	0.102	-3.991

Table 6.3

$$E_1 = 30\text{mV}; E_2 = 40\text{mV};$$

$$D_{\text{Cu}} = 1.586 \times 10^{-3} \text{cm}^2/\text{Sec.}$$

Time (Sec.)	Amps. x $10^{-3}$	log I.
0	1.242	-2.905
62	0.835	-3.078
124	0.631	-3.199
186	0.485	-3.313
248	0.378	-3.421
310	0.301	-3.521
372	0.242	-3.615
434	0.192	-3.715
496	0.155	-3.808
558	0.135	-3.866

Table 6.4

$$E_1 = 40\text{mV}; E_2 = 50\text{mV};$$

$$D_{\text{Cu}} = 1.488 \times 10^{-3} \text{cm}^2/\text{Sec.}$$

Time (Sec.)	Amps. x $10^{-3}$	log I.
0	1.203	-2.919
62	0.835	-3.078
124	0.660	-3.179
186	0.524	-3.280
248	0.417	-3.379
310	0.330	-3.481
372	0.271	-3.565
434	0.223	-3.651
496	0.184	-3.734
558	0.155	-3.808
620	0.126	-3.898
682	0.106	-3.971
744	0.087	-4.058



List of Tables

Table		Page
1.	A list of some nonstoichiometric solids in which chemical diffusivity was measured electrochemically	9
2.	Variation of current with time	26
3.	Variation of current with time	27
4.	Variation of chemical diffusivity with activity	28
5.	$\bar{D}_{Cu}$ , $D_{Cu}(\text{self})$ , $(\frac{d \ln a_{Cu}}{d \ln c_{Cu}})$ and $\delta$ as a function of activity	34
6.	$D_{Cu}$ for pump in and pump out experiments	35

Table 6.23

$$E_1 = 40 \text{ mV}, \quad E_2 = 10 \text{ mV},$$

$$D_{\text{Cu}} = 2.311 \times 10^{-3} \text{ cm}^2/\text{sec}.$$

Time (sec.)	Amps. x $10^{-3}$	log I
0	4.160	-2.380
62	2.720	-2.565
124	1.920	-2.716
186	1.360	-2.866
248	0.960	-3.017
310	0.640	-3.193
372	0.480	-3.318
434	0.384	-3.415
496	0.240	-3.619
558	0.160	-3.795

## CHAPTER 1

### INTRODUCTION

The high temperature corrosion of copper and copper alloys in sulfur containing atmospheres is of importance and interest. Cuprous sulfide is often an important product of such reactions. Where a cuprous sulfide layer is the product of a high temperature reaction, the reaction rate is often fixed by the chemical diffusivity of copper in cuprous sulfide<sup>1,2,3</sup>. The high temperature reduction of sulfides by reducing agents such as hydrogen is of importance in high temperature chemistry and extractive metallurgy. The rate of such reduction reactions is considerably influenced by the chemical diffusivity of the metal in the sulfide<sup>4</sup>.

Cuprous sulfide ( $\text{Cu}_2\text{S}$ ), often known as chalcocite, is a non-stoichiometric compound which is metal deficient. At  $400^\circ\text{C}$ , the non-stoichiometry range extends from  $\text{Cu}_{1.9996}\text{S}$  to  $\text{Cu}_{1.93}\text{S}$ <sup>5</sup>. The defect structure has copper vacancies compensated by electron holes..

The present study is a determination of the chemical diffusivity of copper in chalcocite at  $400^\circ\text{C}$  as a function of the activity. A potentiostatic electrochemical technique has been used. The Cu/S ratio in cuprous sulfide as

a function of the copper activity has also been determined. The following electrochemical cell has been used in the investigation,



where cuprous bromide serves as a solid electrolyte in which copper ions carry the current.

## CHAPTER 2

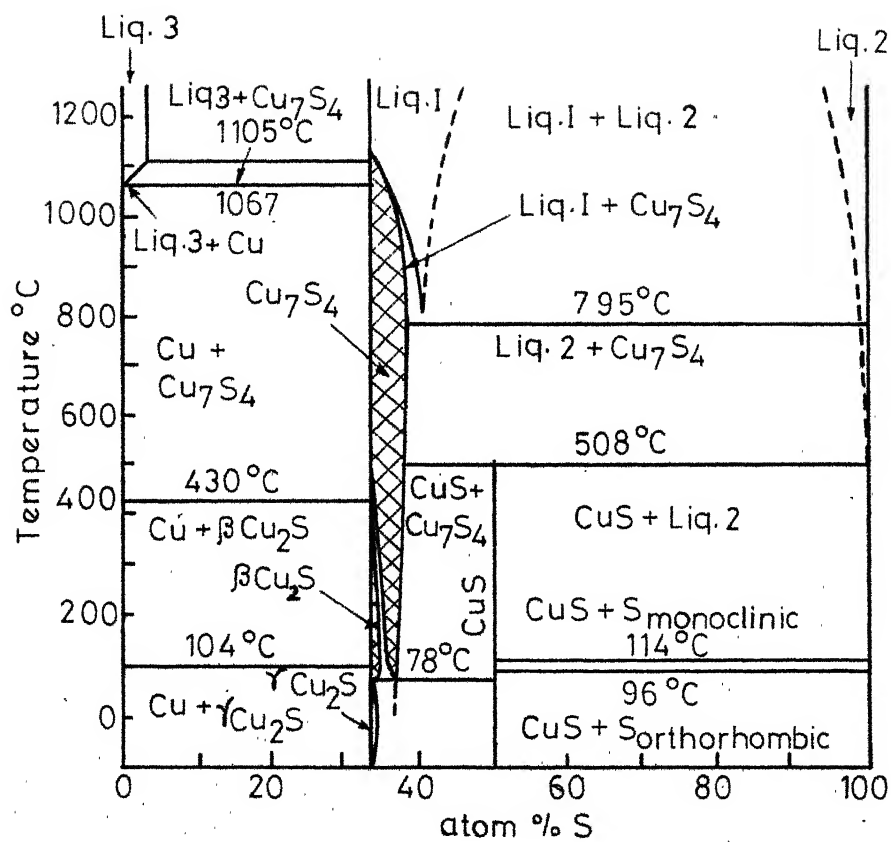
### LITERATURE SURVEY

#### 2.1 The Cu-S phase diagram

A recent phase diagram of the Cu-S system is shown in Fig. 1. The phase diagram has been studied by several workers<sup>6,7</sup>. Sulfur has a finite solubility in copper, depending on the temperature. Copper and sulfur react to form a number of phases.

The Homogeneity range of cuprous sulfide (chalcocite) at 400°C extends from a copper to sulfur ratio of  $1.9996 \pm 0.0002$  for samples co-existing with metallic copper to a ratio less than 1.93 for samples co-existing with digenite ( $\text{Cu}_{1.8}\text{S}$ )<sup>5</sup>. This range of non-stoichiometry is accommodated through the formation of cationic vacancies in the lattice. Charge neutrality may be pictured to occur by the conversion of some of the cuprous ions into cupric ions or by the formation of electron holes. The latter is energetically favoured in copper rich cuprous sulfide<sup>8</sup>.

Studies on the resonance phenomena of the copper nucleus in  $\text{Cu}_x\text{S}$  ( $1.85 < x < 2$ ) shows that an orthorhombic modification ( $\gamma$ -phase) transforms into a hexagonal form ( $\beta$ -phase) at 103°C and further transforms into a cubic ( $\alpha$ -modification) at 435°C.<sup>9</sup> Various other



Phase diagram for the Cu-S system

Fig. 1

phase transitions in <sup>Copper Sulphide</sup> chalcocite are reported by several workers<sup>10,11,12</sup> from conductivity, Hall effect and Seebeck effect data for different temperatures. The hexagonal nature of chalcocite at 400°C is reported by different authors.<sup>13,14</sup>

## 2.2 Electrical properties of chalcocite

Cuprous sulfide is a non-stoichiometric compound consisting of monovalent copper ions and divalent sulfur ions. At 400°C, at least half of the copper ions are distributed virtually at random among a large number of nearly equivalent lattice sites according to X-ray investigation.<sup>15</sup> This is consistent with the relatively high value of the self diffusion coefficient of copper ion ( $9 \times 10^{-6} \text{ cm}^2/\text{sec.}$  at 420°C)<sup>16</sup> and ionic conductivity ( $0.20 \text{ ohm}^{-1} \text{ cm}^{-1}$  at 400°C).<sup>17</sup> The disorder of sulfur ions seems to be negligible in view of their large size and their extremely low diffusivity.<sup>18</sup>

The electrical properties of chalcocite ( $\beta$ -modification having Hexagonal structure stable at 400°C) have been investigated by Kushida, Hirahara, Eisenmann and many others<sup>19,20,21,22</sup>. According to Hirahara cuprous sulfide equilibrated with metallic copper at 400°C has an ionic conductivity  $\sigma_{\text{ion}} = 0.2 \text{ ohm}^{-1} \text{ cm}^{-1}$  and an electronic conductivity  $\sigma_{\text{e}} = 0.16 \text{ ohm}^{-1} \text{ cm}^{-1}$ . Partial ionic conduction

has been shown most directly by the electrolysis of a  $\text{Cu}_2\text{S}$  sample between copper electrodes. Samples which were not equilibrated with copper had apparently higher conductivities and from Hall effect studies it has been shown that under such circumstances p-type conduction predominates. The electronic conductivity  $\sigma_p$ , of  $\text{Cu}_{2-\delta}\text{S}$  at different copper activities was determined by Wagner and Wagner<sup>5</sup>. The total conductivity of chalcocite increases notably with copper deficiency ( $\sigma = 10^{-2} \rightarrow 50 \text{ ohm}^{-1} \text{ cm}^{-1}$ )<sup>20,21</sup> at room temperature. Digenite and Covellite (sulfur rich modification of cuprous sulfide) are almost metallic in character ( $\sigma = 2 \times 10^4 \text{ ohm}^{-1} \text{ cm}^{-1}$ )<sup>21,23</sup> at room temperature. This behaviour must be associated with the increased production of electron holes with copper deficiency and the large mobility values associated with electron holes in comparison with copper ions.

In view of the high degree of disorder of copper ions in cuprous sulfide  $\text{Cu}_2\text{S}$  of ideal composition, the chemical potential of copper ions is essentially independent of small deviations from the ideal Cu/S ratio. Small deviations from the ideal composition correspond to low concentrations of electron holes. The laws of dilute solutions can be applied under such circumstances. A theoretical analysis based on the above concept shows that



the copper deficit increases slightly with increasing temperature<sup>5</sup>. This holds good for cuprous sulfide co-existing with metallic copper where the copper deficit is very small. For a relatively large deficit of copper, the concentration of electron holes is large and the laws of dilute solution cannot be applied. Under such circumstances the behaviour of the system can be fairly explained by using a quantum mechanical - free electron-gas theory<sup>5</sup>.

Electrical conduction in cuprous sulfide is due to both electronic carriers and ionic carriers. Electronic conduction in chalcocite is supposedly due to both excess electrons and electron holes whose concentration depends upon the stoichiometry of cuprous sulfide, the temperature and the impurity content.<sup>11</sup> In chalcocite the sulfur ion mobility is considered negligible in comparison with the copper ion mobility and the ionic contribution towards electrical conduction is exclusively due to cuprous ions. There is experimental evidence to support this view point<sup>24,25</sup>.

### 2.3 Chemical diffusion in non-stoichiometric compounds

For many binary compounds the diffusion rates of the two components may differ by many powers of ten. It is appropriate then to consider that only one component

i is mobile and involved in the homogenization process. Thus for example in chalcocite copper ions are mobile and sulfur ions are stationary. The homogenization of cuprous sulfide sample in which there is a gradient of copper concentration, can be described by the chemical diffusion coefficient of copper. This is a measure of the simultaneous transport of copper ions and electrons in the lattice.

The chemical diffusion coefficient  $\tilde{D}_i$  is related to the self diffusion coefficient  $D_i$ , obtained from the radioactive tracer measurement by the Darken equation<sup>26,27</sup>

$$\tilde{D}_i = D_i \left( \frac{\partial \ln a_i}{\partial \ln C_i} \right) \quad (2.1)$$

Where the second term on the right hand side is a thermodynamic factor which is dependent on the activity  $a_i$  and the concentration  $C_i$  of the species 'i'. This factor may be quite large and thus the chemical diffusion coefficient can be many times greater than self diffusion coefficient<sup>26</sup>. It is also interesting to note that the chemical diffusion coefficient values given by the Darken equation and the experimental values need not be in agreement. The Darken equation allows one to predict approximately the chemical diffusion coefficient for small

deviation from stoichiometry. The equation often does not give correct values at large deviations from stoichiometry. This behaviour was observed in Wüstite and the presence of ordered complexes in  $\text{FeO}_x$  has been proposed as a possible cause of the discrepancy.<sup>28</sup> Similar ordering phenomena have also been reported in cuprous sulfide.<sup>29</sup>

From recent studies<sup>26</sup> on the chemical diffusion coefficients in compounds, it seems that the measured chemical diffusion coefficient decreases as the concentration of the predominant defect increases. This behaviour is typical of many non-stoichiometric compounds.<sup>29</sup> However, chemical diffusion data are available only for a few compounds and it is obviously desirable to find out whether many other non-stoichiometric compounds behave in this way. It would also be useful to find new methods for measuring the coefficients. In the usual methods, the non-stoichiometric compound is initially held in equilibrium with a surrounding gas mixture which fixes the component activities in the compound. A step change is then made in the composition of the gas mixture and some physical property such as weight, electrical conductivity, the position of a colour front or p-n junction is recorded with time as the composition of the specimen begins to change to a new equilibrium value. While

Table 1

Compound Studied	Investigator
$\text{Fe}_{1-\delta} \text{O}$	H. Rickert
$\text{L-Ag}_{2+\delta} \text{S}$	H. Rickert
$\text{L-Ag}_{2+\delta} \text{Se}$	H. Rickert
$\text{L-Cu}_{2-\delta} \text{S}$	K. Wiss
$\text{Ce}_{\text{e}} \text{O}_{2-x}$	B.C.H. Steele
$\text{U O}_{2+x}$	B.C.H. Steele

these methods can produce reliable data it has often been observed that the reaction at the gas/solid interface may be rate controlling or at least make a significant contribution to the overall rates. This effect will usually be greater when the chemical diffusion coefficients have large values ( $>10^{-6} \text{ cm}^2/\text{sec.}$ ) and under these circumstances interpretation of the experimental results can be very difficult<sup>26</sup>. The electrochemical technique is superior to the methods discussed above because (a) stepwise changes in the activity can be made more quickly and correctly and (b) interference from side reactions is minimised. The electrochemical technique has been

applied to the determination of diffusivities in liquid and solid metals<sup>30</sup> and in non-stoichiometric compounds<sup>31,27</sup>. Table 1 lists some of the non-stoichiometric solids in which chemical diffusivity measurements were carried out electrochemically.

Different electrochemical techniques have been used for the determination of chemical diffusion coefficients in non-stoichiometric compounds at various composition and temperature. These include potentiostatic, galvanostatic and potentiometric techniques. The measurements can be made over narrow ranges of composition. Such measurements show that the chemical diffusion coefficient is concentration dependent in many oxide systems ( $\text{CeO}_{2-x}$ ,  $\text{UO}_{2+x}$ ). In these oxide systems, the self diffusion coefficients are directly proportional to the defect concentration, whereas the chemical diffusion coefficients are inversely proportional to the defect concentration<sup>27</sup>.

## CHAPTER 3

### THEORETICAL CONSIDERATIONS

The solid state potentiostatic electrochemical technique used in the present investigation is similar to that used by Chu, Rickert and Weppner<sup>27</sup> to study the chemical diffusivity of iron in Wüstite. The electrochemical cell may be represented as



Cuprous bromide is essentially an ionic conductor between 350 and 450°C when subjected to a polarizing potential of less than 0.3 volt<sup>5</sup>. A similar electrochemical cell was used by K. Wiss (32) to determine the chemical diffusion coefficient of Copper in ~~dégenite~~ <sup>malachite</sup> at 440 and 460°C.

#### 3.1 Potential static method using a single cell:

A fixed activity and hence a fixed concentration of copper in cuprous sulfide can be established at the copper bromide/copper sulfide interface by applying a preselected voltage across cell (A) with the sulfide at the +ve polarity. At equilibrium a uniform copper activity is attained all through the copper sulfide specimen and

this activity is related to the applied voltage by

$$E_{\text{appl}} = \frac{-RT}{F} \ln a_{\text{Cu}} \quad \dots \quad (3.1)$$

The copper concentration at the copper sulfide/copper bromide interface may now be quickly changed to a new value by increasing or decreasing the applied voltage across the cell (A). The diffusion of copper out of copper sulfide or into the copper sulfide then becomes essential to establish the new equilibrium conditions determined by the final voltage. This gives rise to a diffusion controlled current in the external circuit of cell (A) as a function of time. The current time plot may be analysed using the pertinent solution to Fick's second law in order to obtain the diffusivity of copper. Fick's second law for the present case may be written as

$$\frac{\partial C_{\text{Cu}}}{\partial t} = D_{\text{Cu}} \left( \frac{\partial^2 C_{\text{Cu}}}{\partial x^2} \right) \quad \dots \quad (3.2)$$

The initial and boundary conditions are:

$$C_{\text{Cu}} = C_{\text{Cu}}^1, \quad 0 \leq x \leq 1, \quad t = 0;$$

$$C_{\text{Cu}} = C_{\text{Cu}}^{11}, \quad x = 0, \quad t > 0.$$

$$\left( \frac{\partial C_{\text{Cu}}}{\partial x} \right)_{x=1} = 0$$

The solution to Eq. 3.2 is: <sup>33,34</sup>

$$\frac{C'_{Cu} - C_{Cu}}{C''_{Cu} - C_{Cu}} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \exp \left( - \frac{(2n+1)^2 \pi^2 \tilde{D}_{Cu} t}{4l^2} \right) \times$$

$$\sin \frac{(2n+1)\pi x}{2l} \quad (3-3)$$

If  $M_t$  denotes the total amount of Copper which has entered the copper sulfide specimen at time 't' and  $M_{\infty}$  the corresponding amount after infinite time <sup>34</sup>,

$$\frac{M_t}{M_{\infty}} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp - \left[ (2n+1)^2 \pi^2 \frac{\tilde{D}_t}{4l^2} \right] \quad \dots (3.4)$$

For sufficiently long times, one may just take the first term in the summation and write

$$\frac{M_t}{M_{\infty}} \approx 1 - \frac{8}{\pi^2} \exp - \left( \pi^2 \frac{\tilde{D}_t}{4l^2} \right) \quad \dots (3.5)$$

$M_{\infty}$  is given by

$$M_{\infty} = \pi a^2 l (C'_{Cu} - C''_{Cu}) \quad \dots (3.6)$$

where  $a$  is the diameter of the copper sulfide specimen

$M_t$  is given by

$$M_t = \frac{1}{F} \int_0^t I \, dt \quad \dots (3.7)$$

where  $I$  is the current in the external circuit.

Upon inserting Eqs. (3.6) and (3.7) into Eq. (3.5) and differentiating with respect to time, one obtains

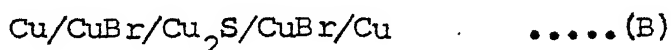
$$I = 2F \pi^2 a^2 D \left( \frac{C'_{Cu} - C''_{Cu}}{l} \right) \exp \left( - \pi^2 \frac{\tilde{D}_t}{4l^2} \right) \dots (3.8)$$



From the slope of the  $\log I$  Vs.  $t$  plot at long times, the diffusivity may be calculated using Eq. (3.8).

### 3.2 Double cell method:

The galvanic cell used in this method is given below.



The cell circuitry is given in Fig.(2). Initially a voltage  $E_1$ , was applied with the potentiostat and a uniform copper activity (corresponding to  $E_1$ ) was attained in the copper sulfide. At the start of an experimental run, the electro motive force was changed to a new value  $E_2$ . This resulted in the diffusion of copper into or out of the cuprous sulfide specimen. The diffusion current may be analysed to obtain the chemical diffusivity of copper, as explained below:

The initial and boundary conditions are

$$C_{\text{Cu}} = C'_{\text{Cu}} \quad 0 < x < 1, \quad t = 0 \quad (\text{Corresponding to } E_1)$$

$$C_{\text{Cu}} = C''_{\text{Cu}} \quad x = 0 \text{ and } x = 1, \quad t > 0 \quad (\text{Corresponding to } E_2)$$

$$C_{\text{Cu}} = C''_{\text{Cu}} \quad \text{for all } x, \quad t = \infty$$

The solution to Fick's second law corresponding to the above set of conditions is given by <sup>33,34,35</sup>

For sufficiently large values of  $t$ , only the first term in the summation in Eq. (3.15) makes a significant contribution. Hence at long times

$$I = \frac{4FA\tilde{D}_{cu}}{l} (C''_{cu} - C'_{cu}) \exp\left(-\frac{\pi^2 \tilde{D}_{cu} t}{l^2}\right) \dots (3.16)$$

Equation (3.16) holds for diffusion across one interface of cell (B). Since diffusion occurs across both interfaces, the current,  $I$ , must be twice the value indicated by Eq. (3.16).

Making this correction, we get,

$$I = \frac{8FA\tilde{D}_{cu}}{l} (C''_{cu} - C'_{cu}) \exp\left(-\frac{\pi^2 \tilde{D}_{cu} t}{l^2}\right) \dots (3.17)$$

Taking logarithms of both sides

$$\log I = \log \left[ \frac{8FA\tilde{D}_{cu}}{l} (C''_{cu} - C'_{cu}) \right] - \frac{\pi^2 \tilde{D}_{cu} t}{2.303 l^2} \dots (3.18)$$

Thus at long times a plot of  $\log I$  Vs. ' $t$ ' gives a straight line whose slope will be  $\frac{-\pi^2 \tilde{D}_{cu}}{2.303 l^2}$  and from which the chemical diffusivity can be obtained. The ordinate interval can also be used for the determination of  $\tilde{D}_{cu}$ , for which, however, the knowledge of  $(C''_{cu} - C'_{cu})$  is necessary.

### 3.3 Coulometric titration

The activity of copper in cuprous sulfide as a function of the copper to sulfur ratio was determined using a coulometric titration technique. When a known

current  $I$  is passed through cell (A) for a known period of time, a definite quantity of copper will either get pumped into the cuprous sulfide or out of it depending on the deviation of current according to Faraday's law. The quantity of copper getting into the cuprous sulfide or out of it is directly proportional to the quantity of electricity passed. The chemical potential of copper  $\mu_{\text{Cu}}$  in cuprous sulfide in cell (A) is related to the electromotive force  $E$  by

$$\mu_{\text{Cu}} - \mu_{\text{Cu}}^{\circ} = -EF \quad \dots \quad (3.20)$$

where  $\mu_{\text{Cu}}^{\circ}$  is the chemical potential of copper in its standard state

When cell A is shorted or a positive potential of a few millivolts ( $\approx 0$ ) is forced across the cell with the help of a potentiostat the cuprous sulfide sample nearly attains the equilibrium composition of cuprous sulfide co-existing with metallic copper. A well-defined amount of copper may now be removed from the sample by passing a current  $I$  through the cell for a period ' $t$ '. The decrease ' $\delta$ ' in the Cu/S ratio in cuprous sulfide with respect to the sample with unit activity of copper is given by,

$$\delta = \frac{q}{n_s F} \quad \dots \quad (3.21)$$

$$\text{i.e., } \delta = \frac{It}{n_s F} \quad \dots \quad (3.22)$$

where  $q$  is the number of coulombs of charge passing through the cell (A) and  $n_s$  is the number of gram atoms of sulfur in the cuprous sulfide sample. The value of  $n_s$  can be calculated from a knowledge of the weight of the cuprous sulfide electrode under use.

After passing current,  $I$ , for time ' $t$ ' the cell circuit is broken and the open circuit voltage is allowed to attain a constant value. This gives the value of  $E$  for a given value of  $\delta$ . The experiment is repeated in order to obtain a plot of  $E$  vs  $\delta$ . The plot may be used to calculate the thermodynamic factor of Cu in cuprous sulphide as explained in chapter 5. The thermodynamic factor relates the chemical diffusivity with the self diffusivity.

## CHAPTER 4

### EXPERIMENTAL MATERIALS AND PROCEDURE

#### 4.1 Materials

Two grades of chalcocite were used for the experiment. The first grades (Cerac/pure incorporated MenoMonee Falls, Wisconsin) was of 99.5% purity and the second grade (PolyResearch Corporation N.Y. 11803) was of 99.999% purity. The nature of the impurities present or the method of preparation of the reagent was not specified by the supplier.

High purity copper powder (99.95%) and cuprous bromide (99.95%) were used in the experiment.

Commercial argon was purified by passing first through anhydrous calcium chloride to remove moisture and then through an activated copper catalyst (BASF) kept at  $180 \pm 10^{\circ}\text{C}$  (to remove any free oxygen) and then admitted into the furnace containing the solid state electrochemical cell (A or B). Purified argon provided the desired inert atmosphere for the experiment. The BASF catalyst was regenerated periodically after several weeks of operation by reducing with hydrogen at  $200^{\circ}\text{C}$ .

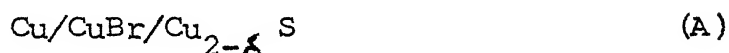
#### 4.2 Furnace

A Kanthal-wound horizontal furnace was used in the experiments (Fig. 3a). The temperature of the cell was

selected from the power supply by turning the ten turn pot and using an ECIL EA 814 electrometer to measure the selected voltage.

#### 4.4 Cell Assembly

In the galvanic cell.



The electrode and electrolyte materials were kept in the form of cylindrical pellets. Copper powder was pressed into a pellet of 1 cm diameter and nearly 0.4 cm thickness by using a hydraulic press and applying a pressure of 10-12 t.s.i. cuprous bromide pellet was also made in the same way with a thickness of 0.2 - 0.3 cm. Cuprous sulfide (of length 0.8 - 2 cm) was pressed by applying a little higher pressure (~15 t.s.i.).

The electrodes and electrolytes were assembled in a slot cut in an alumina tube which could be easily inserted into the furnace (Fig. 3b). Electrical contact with the electrodes was made by means of platinum discs. Platinum lead wires were welded on to the platinum discs. The electrodes and electrolyte could be kept under intimate contact by means of an alumina push rod which could be tightened by means of a brass screw.

#### 4.5a. Potential static single cell technique

The cell, Pt/Cu/CuBr/Cu<sub>2</sub>-S/Pt - (A) was assembled in the alumina holder and inserted into the furnace. The alumina tube holding the cell holder was then evacuated using a 'Duo Seal' vacuum pump down to 50 millitorr pressure. The pressure was measured by a thermocouple gauge. The system was then filled with purified argon. The operation of evacuating down to 50 millitorr and flushing with purified argon was repeated five to six times. Finally, a low flow rate of a few bubbles of argon per minute was maintained.

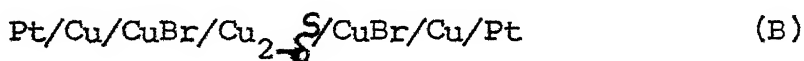
The cell was now heated to a temperature of 400°C. The temperature was controlled to within  $\pm 1^\circ\text{C}$  by means of the Electromax controller.

A low voltage in the range, 10-30 mV, was selected on the regulated power supply and checked using the ECIL EA 814 vibrating condenser electrometer. The selected voltage was applied across cell (A) with the sulfide at positive polarity. Sufficient time was allowed for the current in the circuit (recorded using a sargent recorder) to drop to a zero value. When the current had dropped to zero, the open circuit voltage of cell (A) must be equal to the applied voltage. This was checked by breaking the cell circuit and measuring the open circuit

voltage with the electrometer. Now the copper sulfide sample has a uniform copper activity (or copper concentration) throughout corresponding to the applied voltage. A slightly higher voltage was now selected and applied across the cell (with the sulfide at positive polarity). Simultaneously the current in the circuit was measured as a function of time using the sargent recorder. The current time plot was analysed to determine the chemical diffusivity of copper. A further voltage step was now given and a new current-time plot was recorded. The voltage step was 10, 20 or 30 mV. The highest voltage applied was 130 mV. At the higher voltages, the current never dropped to a zero value, but only to a constant value, presumably because of a steady-state vaporisation of sulfur from the copper sulfide (at higher voltage, the sulfur activity is higher). When this happened, the final constant current was subtracted from the total current and the resulting current - time plot was analysed to obtain the diffusivity.

#### 4.5b. Potentiostatic double cell technique

The following cell was used in the double cell technique:



The circuit used is shown in Fig. 2.



In this experiment diffusion occurs from both faces of the cuprous sulfide specimen. In other details, the experiment is similar to the single cell technique.

#### 4.6 Coulometric titration

The cell,  $\text{Cu/CuBr/Cu}_{2-x}\text{S}$  (A) was assembled in the cell holder. A thin cuprous sulfide sample (0.2-0.3 mm thick) was used. A uniform initial copper activity was established in the cuprous sulfide by applying a voltage of 10 mV using the regulated power supply. The applied voltage was now cut off and a constant current of about 2 mA. was passed through the cell (so as to remove copper from the cuprous sulfide) for a few minutes. The cell current was now broken and the open circuit voltage was measured as a function of time, until the voltage reached a steady value. This value was now noted. A constant current was again passed and the experiment repeated as before. In this way the change in the Cu/S ratio in cuprous sulfide as a function of voltage (open circuit) could be measured upto about 200 mV.

## CHAPTER 5

### RESULTS AND DISCUSSION

#### 5.1 Results

The chemical diffusivity of copper in cuprous sulfide was ascertained from the diffusion current time plot. A mathematical treatment of a purely diffusion controlled electrode process is given in Chapter 3. Equation (3.8) is of particular interest.

$$I = 2F \pi^2 a^2 D_{Cu} \frac{C'_{Cu} - C''_{Cu}}{1} \exp \left( - \pi^2 D_{Cu} t / 4l^2 \right) \quad (3.8)$$

The exponential dependence of current on time is shown in Fig. 5 and tables 2 and 3 for a cell (A) for two sets of ( $E_1$  and  $E_2$ ) values.

A plot of  $\log I$  vs. 't' is a straight line whose slope is  $-\frac{\pi^2 D}{2.303 l^2}$ . Curves showing linear dependence of  $\log I$  on time are shown in Fig. 6. From a knowledge of the slope and the length of the cuprous sulfide electrode, the chemical diffusion coefficient of copper in cuprous sulfide can be computed. Tables 1.1 to 6.23 show the dependence of current on time for various potential ( $E_1$  and  $E_2$ ) steps for cells with different cuprous sulfide electrode thickness.

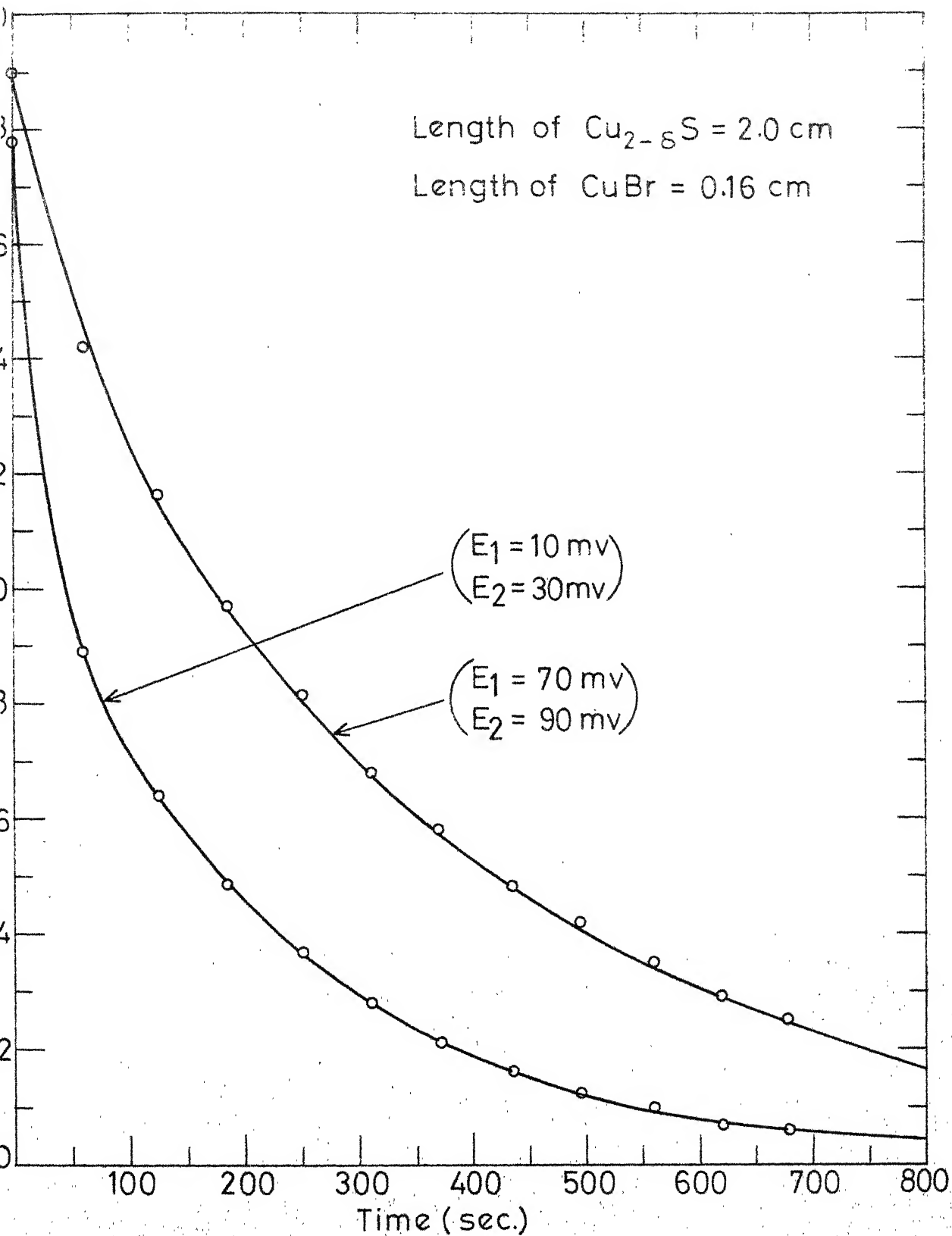
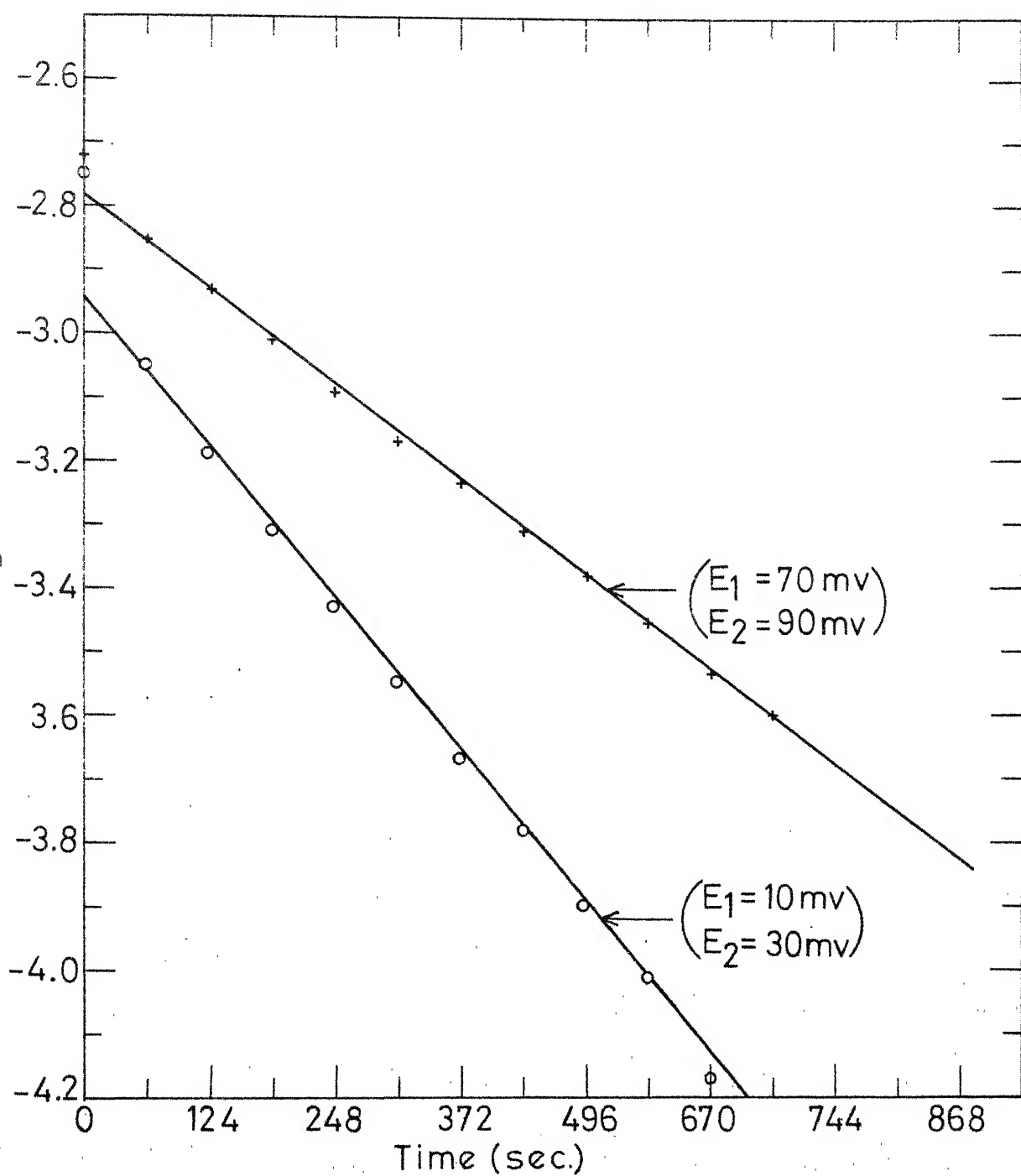


FIG. 5



Log I versus time in the potentiostatic single cell technique

Fig. 6

Table 2

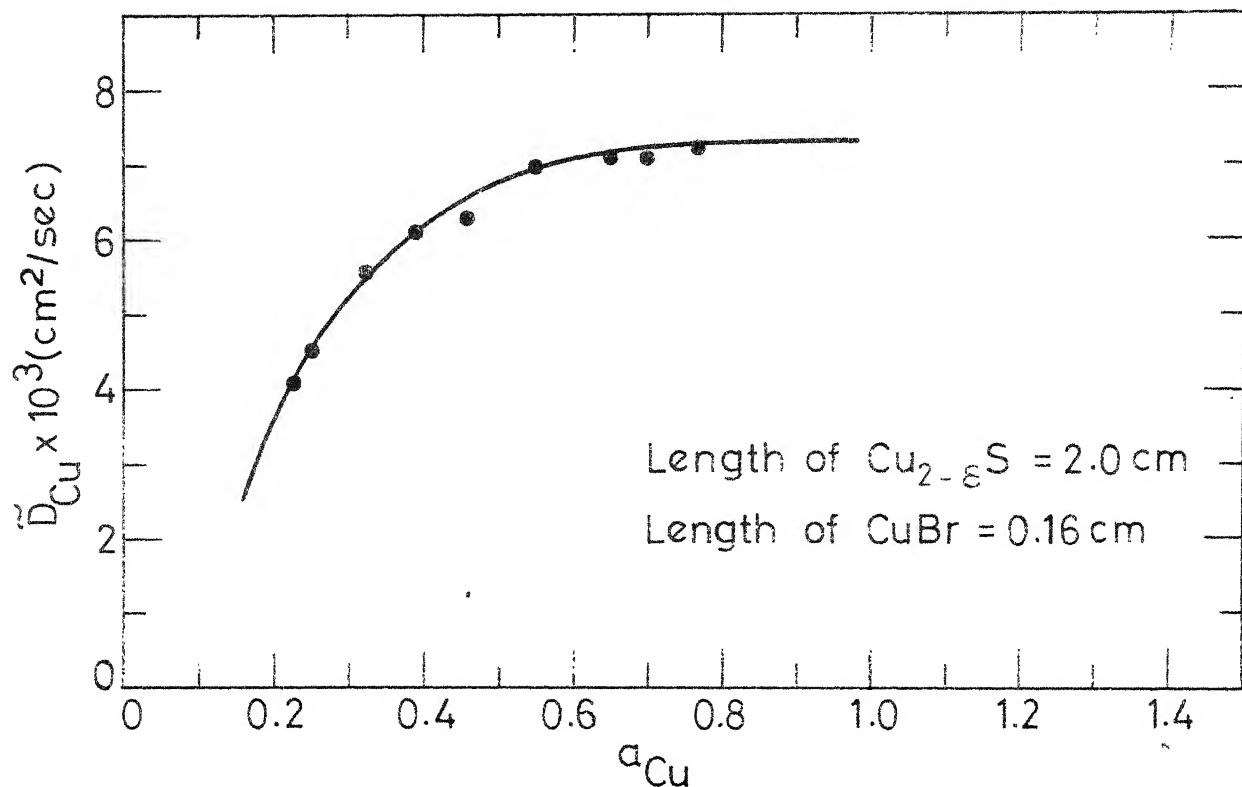
Variation of current with time

Length of  $\text{Cu}_2\text{S}$  electrode = 2.0 cms.

Length of  $\text{CuBr}$  = 0.16 cm

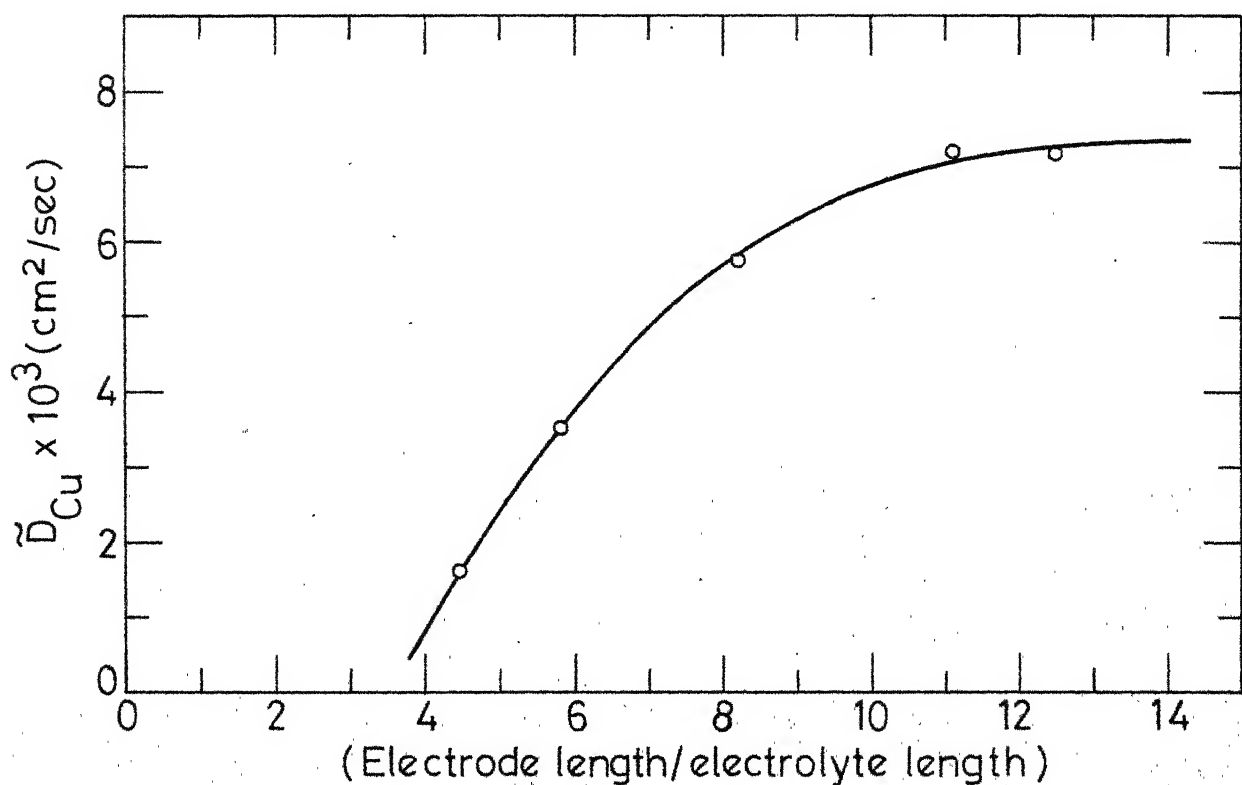
$E_1 = 10$  mV.  $E_2 = 30$  mV.  $D = 7.079 \times 10^{-3}$

Time (Sec.)	Amps. $\times 10^{-3}$	log I
0	1.7767	-2.7503
62	0.8932	-3.0490
124	0.6408	-3.1933
186	0.4855	-3.3139
248	0.3690	-3.4330
310	0.2816	-3.5504
372	0.2136	-3.6704
434	0.1651	-3.7822
496	0.1262	-3.8989
558	0.0971	-4.0128



Chemical diffusion coefficient versus activity of copper in cuprous sulfide at 400 °C

FIG. 7



Chemical diffusion coefficient copper in cuprous sulfide versus ratio of  $\text{Cu}_{2-\delta}\text{S}$  length to  $\text{CuBr}$  length at 400 °C.

FIG. 8

The chemical diffusivity values for various cells show that there is a dependence of the chemical diffusivity on the length ratio of the cuprous sulfide electrode to the electrolyte. This dependence is shown in Fig. 8 where the chemical diffusivity is plotted against the ratio of the electrode/electrolyte lengths. As the ratio ~~of the electrode/electrolyte~~ increases, the chemical diffusivity also increases but reaches a nearly constant value at very large electrode/electrolyte ratios.

## 5.2 Discussion

The observed dependence of the chemical diffusivity on the electrode/electrolyte length ratio could be due to the internal resistance of the cell<sup>36</sup>. This effect may be termed resistance polarisation<sup>38</sup>. Basically, this means that diffusion in the electrolyte is influencing the measured diffusivity values in the electrode. It would be reasonable to expect that this influence would decrease when the ratio of the length  $\text{Cu}_2\text{S}/\text{CuBr}$  increases. This effect is clearly shown in Fig. 8. A further evidence to support this is obtained from the results of the potentiostatic double cell technique. The diffusion coefficient obtained from the experiment corresponds to a value comparable to that

obtained from a single cell with half the electrode length as shown in tables 6.1 to 6.23.

The chemical diffusivity  $\bar{D}_{\text{Cu}}$ , decreases as the copper activity in the cuprous sulfide decreases. This most probably denotes a decreasing thermodynamic factor as the copper content in cuprous sulfide decreases. A similar effect was observed by Hartmann, Rickert and Schendler<sup>58</sup> who studied the chemical diffusivity of silver in silver sulfide.

The thermodynamic factor may be calculated from the results of the coulometric titration experiments. In cuprous sulfide co-existing with metallic copper, the ratio of the number of gram atoms of copper to sulfur is given by<sup>5</sup>

$$\frac{n^{\circ}\text{Cu}}{n_{\text{S}}} \approx 2 \quad (5.1a)$$

where  $n^{\circ}\text{Cu}$  and  $n_{\text{S}}$  are the number of gram atoms of copper and sulfur in cuprous sulfide co-existing with metallic copper or

$$\frac{C^{\circ}_{\text{Cu}}}{C_{\text{S}}} \approx 2 \quad (5.1b)$$

where  $C^{\circ}_{\text{Cu}}$  and  $C_{\text{S}}$  are the concentration in moles/cm<sup>3</sup> of copper and sulfur in cuprous sulfide co-existing with metallic copper. For this case,  $\delta$ , the deviation from stiochiometry, is zero. When there is copper deficiency ( $\delta > 0$ )



$$\frac{C_{Cu}}{C_s} = (2 - \delta) \quad (5.2)$$

$$\ln C_{Cu} = -\ln C_s + \ln (2 - \delta) \quad (5.3)$$

Since  $C_s$  is a constant we have

$$d \ln C_{Cu} = d \ln (2 - \delta) \quad (5.4)$$

$$d \ln C_{Cu} = - \frac{d\delta}{2-\delta} \quad (5.5)$$

but for cell (A),

$$E = \frac{-RT}{F} \ln a_{Cu} \quad (5.6)$$

$$dE = \frac{-RT}{F} d \ln a_{Cu} \quad (5.7)$$

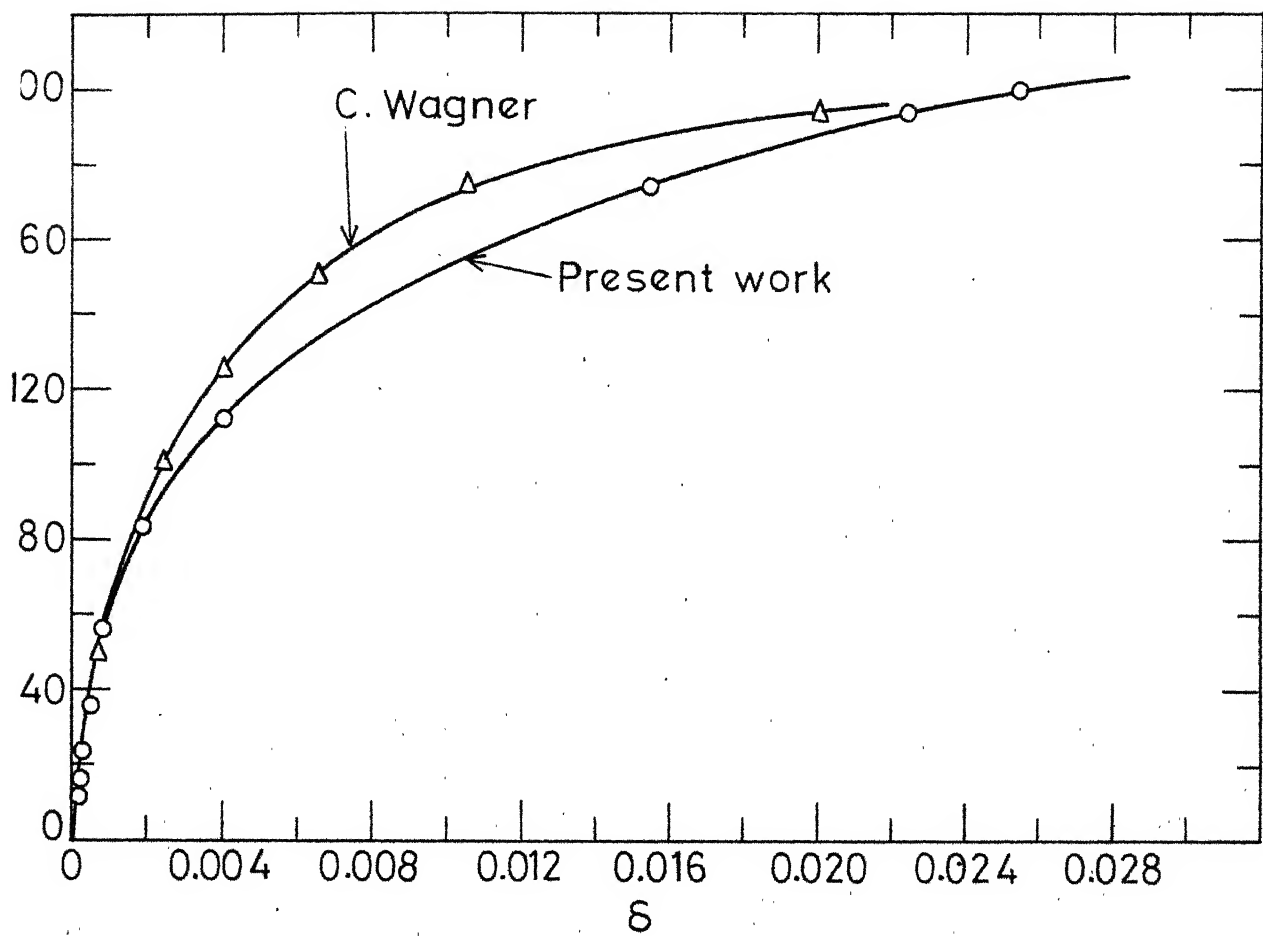
upon combining equations 5.5 and 5.7,

$$\frac{d \ln a_{Cu}}{d \ln C_{Cu}} = \left( \frac{dE}{d\delta} \right) \frac{(2 - \delta) F}{RT} \quad (5.8)$$

The thermodynamic factor, self diffusivity and chemical diffusivity are related through:

$$\tilde{D}_{Cu} = D_{Cu} \frac{d \ln a_{Cu}}{d \ln C_{Cu}} \quad (2.1)$$

A plot of  $E$  versus  $\delta$  obtained from the coulometric titration experiment is shown in Fig. 9. Table 5 gives values of  $\tilde{D}_{Cu}$ ,  $D_{Cu}$  and  $\frac{d \ln a_{Cu}}{d \ln C_{Cu}}$  as functions of the copper activity. The self diffusivity is seen to be nearly independent of the copper activity. A similar effect was observed for silver in silver sulfide<sup>38</sup>.



E versus  $\delta$  plot

FIG. 1

The experimentally determined self diffusivity values<sup>5, 39, 40</sup> may be combined with the thermodynamic factor obtained from the present experiments to calculate the chemical diffusivity values. Such a calculation gives a value of  $\tilde{D}_{\text{Cu}} = 10^{-2} \text{ cm}^2/\text{sec.}$  corresponding to

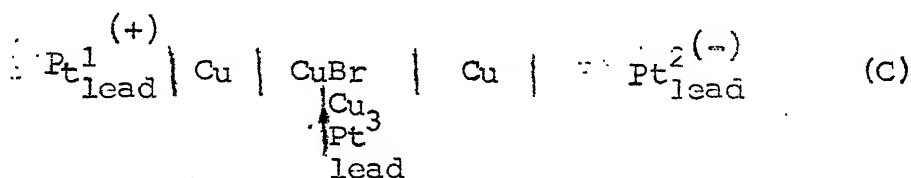
$$a_{\text{Cu}} = 25 \text{ mV.}$$

This is comparable to the experimentally determined value of  $\tilde{D}_{\text{Cu}} = 7 \times 10^{-3} \text{ cm}^2/\text{sec.}$

### 5.3 Polarisation Studies

Apart from the internal resistance of the electrolyte, a time dependent polarisation at the electrode electrolyte interface could also influence the chemical diffusivity measurements.

The polarisation behaviour of Cu/CuBr interface both in the cathodic and anodic processes was studied using the following cell (C) arrangement.



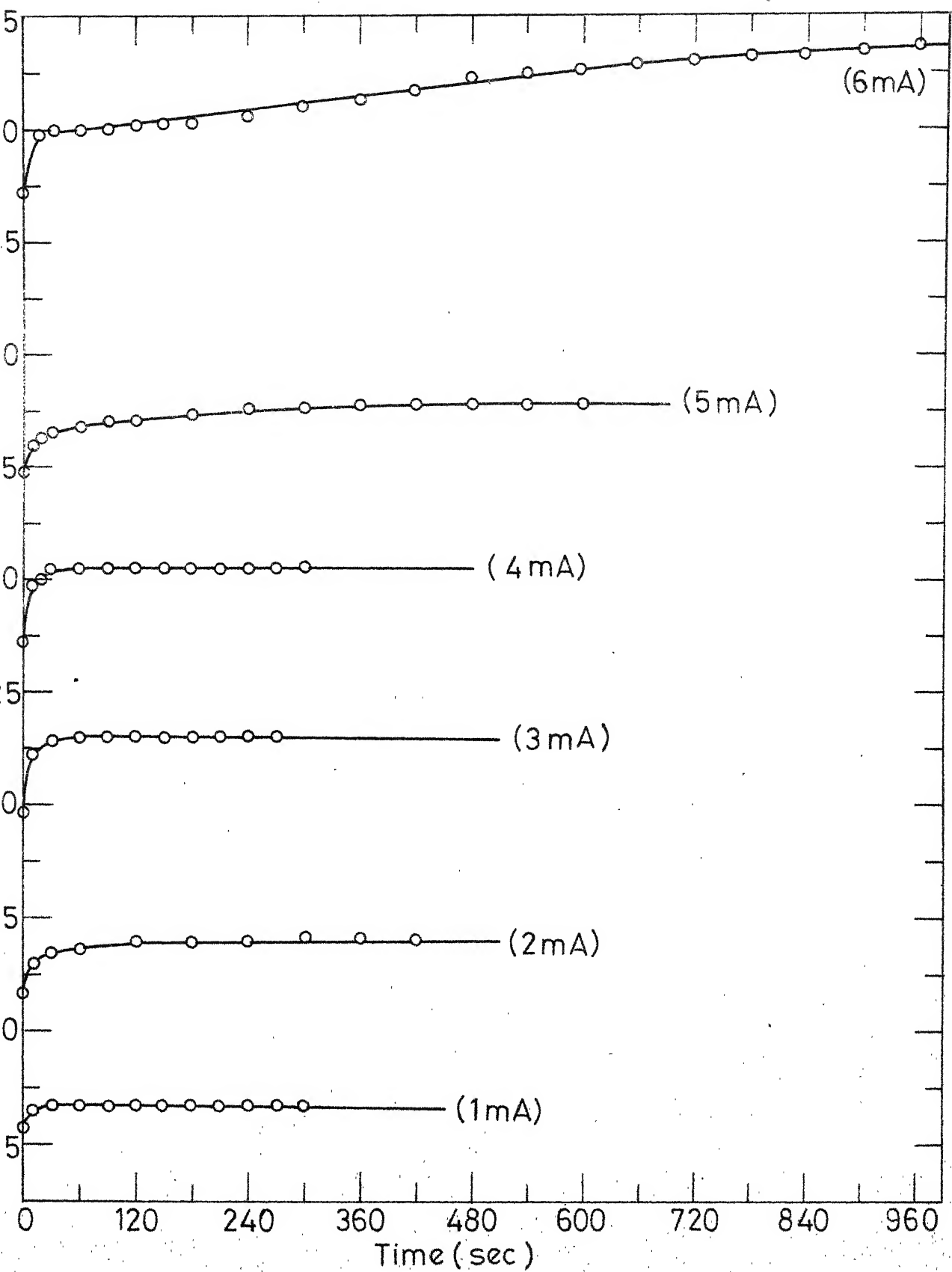
The cell was arranged in the cell holder and maintained at  $400^\circ\text{C}$  inside the furnace.

At the outset the open circuit voltage between  $\text{Pt}^1$  and  $\text{Pt}^3$  and between  $\text{Pt}^2$  and  $\text{Pt}^3$  were measured. A d.c. polarisation current (1-6mA) was now passed through the

platinum leads  $Pt^1$  and  $Pt^2$  with  $Pt^1$  as the positive electrode. These currents are comparable to the diffusion currents encountered in various diffusion experiments. The time dependent polarisation behaviour of the anode was then measured by noting the voltage across  $Pt^1$  and  $Pt^3$  as a function of time. The cathodic polarisation was measured in a similar way by noting the e.m.f. difference between  $Pt^2$  and  $Pt^3$  as a function of time. The total polarisation was also measured by studying the time dependent e.m.f. difference between the electrodes,  $Pt^1$  and  $Pt^2$ . A digital Multimeter (Yamuna Digital Multimeter Model 1010) and a stop watch were used for this purpose.

The anodic voltage as a function of time is shown in Fig. 10. The voltage reaches a constant value within a few seconds after the polarising current is switched on. However, when the polarising current is very large, the voltage continues to increase with time as in the case of 6 mA. This behaviour can be ascribed to void formation at the anode/electrolyte interface caused by the polarisation current. Such void formation has been reported by D.O. Raleigh<sup>37</sup>.

The time dependence of cathodic polarisation behaviour is shown in Fig. 11. The cathodic voltage also reaches a constant value within a few seconds after the polarising current is switched on. Thereafter the polarisation is



Anodic voltage as a function of time in the polarization experiments

FIG.10

"pumpin" curves as shown in table 6. One should prefer the values obtained from the "pumpout" curves.

Table 6

$E_1$ (mV)	$E_2$ (mV)	$\hat{D}_{Cu}$ cm <sup>2</sup> /sec	$E_1$ (mV)	$E_2$ (mV)	$\hat{D}_{Cu}$ cm <sup>2</sup> /sec.
10	20	$7.220 \times 10^{-3}$	20	10	$6.877 \times 10^{-3}$
20	30	$7.089 \times 10^{-3}$	30	20	$6.802 \times 10^{-3}$
30	40	$6.963 \times 10^{-3}$	40	30	$6.594 \times 10^{-3}$
40	50	$6.268 \times 10^{-3}$	50	40	$6.123 \times 10^{-3}$
50	60	$6.068 \times 10^{-3}$	60	50	$6.023 \times 10^{-3}$
60	70	$5.565 \times 10^{-3}$	70	60	$5.476 \times 10^{-3}$

## CHAPTER 6

### SUMMARY AND CONCLUSION

A knowledge of chemical diffusivity as a function of composition is necessary to understand various gas-solid, solid-liquid and solid-solid reactions when transport in the solid is rate-controlling. The chemical diffusivity values of copper in chalcocite were measured as a function of copper activity at 400°C electrochemically. The chemical diffusivity was found to decrease with decrease in the copper activity. It was found that void formation at the anod/electrolyte interface and mass transport in the electrolyte, could influence the measured diffusivity values. The effects could be minimised by using a cathode copper electrode and maintaining a large cuprous sulphide/electrolyte length ratio.

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APPENDIXCELL NO. 1

Length of  $\text{Cu}_2\text{S} = 0.89 \text{ cm}$

Length of  $\text{CuBr} = 0.2 \text{ cm}$

Table 1.1

$E_1 = 10 \text{ mV}; E_2 = 30 \text{ mV}$

$D_{\text{Cu}} = 1.592 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. $\times$ $10^{-3}$	$\log I$
0	1.480	-2.829
62	0.600	-3.221
124	0.340	-3.468
186	0.240	-3.619
248	0.180	-3.744
310	0.160	-3.795
372	0.120	-3.920
434	0.100	-4.000
496	0.080	-4.096

Table 1.2

$E_1 = 30 \text{ mV}; E_2 = 50 \text{ mV}$

$D_{\text{Cu}} = 1.364 \times 10^{-3} \text{ cm}^2/\text{sec}$

Time (sec.)	Amps. $\times$ $10^{-3}$	$\log I$
0	1.660	-2.779
62	0.820	-3.086
124	0.540	-3.267
186	0.380	-3.420
248	0.300	-3.522
310	0.260	-3.585
372	0.180	-3.744
434	0.160	-3.795
496	0.140	-3.853
558	0.140	-3.853
620	0.100	-4.000

Table 1.3

$E_1 = 50 \text{ mV}$ ,  $E_2 = 70 \text{ mV}$ ,  
 $D_{\text{Cu}} = 1.353 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. x $10^{-3}$	log I
0	2.120	-2.673
62	1.040	-2.983
124	0.700	-3.154
186	0.520	-3.284
248	0.400	-3.397
310	0.320	-3.494
372	0.280	-3.552
434	0.240	-3.619
496	0.200	-3.699
558	0.160	-3.795
620	0.160	-3.795

Table 1.4

$E_1 = 70 \text{ mV}$ ;  $E_2 = 90 \text{ mV}$ ;  
 $D_{\text{Cu}} = 1.274 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. x $10^{-3}$	log I
0	2.060	-2.686
62	1.100	-2.958
124	0.740	-3.130
186	0.500	-3.301
248	0.420	-3.376
310	0.300	-3.522
372	0.260	-3.585
434	0.220	-3.657
496	0.180	-3.744
558	0.140	-3.853

Table 1.5

$$E_1 = 90 \text{ mV}; \quad E_2 = 70 \text{ mV}$$

$$D_{\text{Cu}} = 1.194 \times 10^{-3} \text{ cm}^2/\text{sec.}$$

Time (sec.)	Amps. x $10^{-3}$	log I
0	2.640	-2.578
62	1.440	-2.841
124	1.080	-2.966
186	0.880	-3.055
248	0.720	-3.142
310	0.600	-3.221
372	0.480	-3.318
434	0.460	-3.337
496	0.440	-3.356
558	0.440	-3.356

Table 1.6

$$E_1 = 10 \text{ mV}; \quad E_2 = 40 \text{ mV},$$

$$D_{\text{Cu}} = 1.99 \times 10^{-3} \text{ cm}^2/\text{sec.}$$

Time (sec.)	Amps. x $10^{-3}$	log I
0	2.580	-2.588
62	1.100	-2.958
124	0.580	-3.236
186	0.380	-3.420
248	0.260	-3.585
310	0.180	-3.744
372	0.140	-3.853
434	0.100	-4.000
496	0.060	-4.221
558	0.060	-4.221
620	0.040	-4.397

Table 1.11

$E_1 = 20 \text{ mV}; E_2 = 60 \text{ mV};$   
 $D_{\text{Cu}} = 1.876 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. x $10^{-3}$	log I
0	3.220	-2.492
62	1.620	-2.790
124	1.020	-2.991
186	0.700	-3.154
248	0.540	-3.267
310	0.380	-3.420
372	0.300	-3.522
434	0.280	-3.552
496	0.220	-3.657
558	0.180	-3.744
620	0.140	-3.853

Table 1.12

$E_1 = 50 \text{ mV}; E_2 = 90 \text{ mV};$   
 $D_{\text{Cu}} = 1.493 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. x $10^{-3}$	log I
0	4.200	-2.376
62	2.160	-2.665
124	1.440	-2.841
186	1.040	-2.983
248	0.800	-3.096
310	0.600	-3.221
372	0.480	-3.318
434	0.400	-3.397
496	0.320	-3.494
558	0.280	-3.552
620	0.200	-3.699

Table 1.13

$E_1 = 60 \text{ mV}; E_2 = 100 \text{ mV};$   
 $D_{\text{Cu}} = 1.226 \times 10^{-3} \text{ cm}^2/\text{sec}.$

Time (sec.)	Amps. x $10^{-3}$	log I
0	3.860	-2.413
62	2.200	-2.657
124	1.480	-2.829
186	1.080	-2.966
248	0.840	-3.075
310	0.680	-3.167
372	0.560	-3.251
434	0.400	-3.397
496	0.320	-3.494
558	0.280	-3.552

Table 1.14

$E_1 = 10 \text{ mV}; E_2 = 60 \text{ mV};$   
 $D_{\text{Cu}} = 2.388 \times 10^{-3} \text{ cm}^2/\text{sec}.$

Time (sec.)	Amps. x $10^{-3}$	log I
0	3.270	-2.485
62	1.550	-2.809
124	0.950	-3.022
186	0.610	-3.214
248	0.430	-3.366
310	0.310	-3.508
372	0.230	-3.638
434	0.150	-3.823
496	0.110	-3.958
558	0.090	-4.045
620	0.070	-4.154

Table 1.15

$$E_1 = 60 \text{ mV}; \quad E_2 = 110 \text{ mV};$$

$$D_{\text{Cu}} = 1.592 \times 10^{-3} \text{ cm}^2/\text{sec.}$$

Time (sec.)	Amps. x $10^{-3}$	log I
0	4.160	-2.380
62	2.480	-2.605
124	1.640	-2.785
186	1.200	-2.920
248	0.880	-3.055
310	0.640	-3.193
372	0.480	-3.318
434	0.400	-3.397
496	0.320	-3.494
558	0.280	-3.552
620	0.240	-3.719
862	0.200	-3.699



CELL NO. 2

Length of  $\text{Cu}_2\text{S} = 1.08 \text{ cm}$

Length of  $\text{CuBr} = 1.85 \text{ m.m.}$

Table 2.1

$E_1 = 10 \text{ mV}; E_2 = 30 \text{ mV},$   
 $D_{\text{Cu}} = 3.510 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. x $10^{-3}$	log I
0	1.720	-2.764
62	1.080	-2.966
124	0.640	-3.193
186	0.400	-3.397
248	0.220	-3.657
310	0.120	-3.920
372	0.060	-4.221
434	0.040	-4.397

Table 2.2

$E_1 = 30 \text{ mV}; E_2 = 50 \text{ mV.}$   
 $D_{\text{Cu}} = 3.233 \times 10^{-3}$

Time (sec.)	Amps. x $10^{-3}$	log
0	1.380	-2.860
62	0.740	-3.130
124	0.500	-3.301
186	0.340	-3.468
248	0.220	-3.657
310	0.180	-3.744
372	0.140	-3.853
434	0.100	-4.000
496	0.060	-4.221
558	0.060	-4.221

Table 2.3

$E_1 = 50 \text{ mV}; E_2 = 70 \text{ mV};$   
 $D_{\text{Cu}} = 3.233 \times 10^{-3} \text{ cm}^2/\text{sec}.$

Time (sec.)	Amps. x $10^{-3}$	log I
0	1.42	-2.8477
62	0.82	-0.862
124	0.50	-3.301
186	0.34	-3.468
248	0.22	-3.657
310	0.160	-3.795
372	0.10	-4.000
434	0.08	-4.096
496	0.06	-4.221
558	0.06	-4.221

Table 2.4

$E_1 = 70 \text{ mV}; E_2 = 90 \text{ mV};$   
 $D_{\text{Cu}} = 2.194 \times 10^{-3} \text{ cm}^2/\text{sec}.$

Time (sec.)	Amps. x $10^{-3}$	log I
0	1.68	-2.774
62	1.32	-2.879
124	0.68	-3.167
186	0.48	-3.318
248	0.36	-3.443
310	0.28	-3.552
372	0.20	-3.699
434	0.16	-3.795
496	0.12	-3.920
558	0.08	-4.096
620	0.08	-4.096

Table 2.5

$$E_1 = 90 \text{ mV}; \quad E_2 = 110 \text{ mV};$$

$$D_{\text{Cu}} = 2.145 \times 10^{-3} \text{ cm}^2/\text{sec.}$$

Time (sec.)	Amps. x $10^{-3}$	log I
0	1.4	-2.853
62	1.00	-3.000
124	0.76	-3.119
186	0.56	-3.251
248	0.40	-3.397
310	0.32	-3.494
372	0.24	-3.619
434	0.20	-3.699
496	0.16	-3.795
558	0.12	-3.920
620	0.12	-3.9208

Table 2.6

$$E_1 = 110 \text{ mV}; \quad E_2 = 130 \text{ mV};$$

$$D_{\text{Cu}} = 2.633 \times 10^{-3}$$

Time (sec.)	Amps. x $10^{-3}$	log I
0	1.12	-2.950
62	0.8	-3.096
124	0.56	-3.251
186	0.36	-3.443
248	0.316	-3.500
310	0.20	-3.699
372	0.16	-3.795
434	0.12	-3.920
496	0.10	-4.000
558	0.10	-4.000

CELL NO. 3

Length of  $\text{Cu}_2\text{S} = 1.47 \text{ cm}$

Length of  $\text{CuBr} = 0.18 \text{ cm}$

Table 3.1

$E_1 = 10 \text{ mV}; E_2 = 30 \text{ mV};$

$D_{\text{Cu}} = 5.724 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. $\times$ $10^{-3}$	log I
0	1.780	-2.749
62	1.100	-2.958
124	0.820	-3.086
186	0.580	-3.236
248	0.420	-3.376
310	0.300	-3.522
372	0.220	-3.657
434	0.140	-3.853
496	0.100	-4.000
558	0.0600	-4.221
620	0.040	-4.397

Table 3.2

$E_1 = 30 \text{ mV}; E_2 = 50 \text{ mV};$

$D_{\text{Cu}} = 4.507 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. $\times$ $10^{-3}$	log I
0	2.380	-2.623
62	1.520	-2.818
124	1.140	-2.943
186	0.840	-3.075
248	0.660	-3.180
310	0.480	-3.318
372	0.400	-3.397
434	0.3400	-3.468
496	0.240	-3.619
558	0.160	-3.795
620	0.140	-3.853
682	0.120	-3.920

Table 3.3

$E_1 = 50 \text{ mV}; E_2 = 70 \text{ mV};$   
 $D_{\text{Cu}} = 4.55 \times 10^{-3} \text{ cm}^2/\text{sec}.$

Time (sec.)	Amps. x $10^{-3}$	log I
0	3.300	-2.481
62	2.160	-2.665
124	1.600	-2.795
186	1.240	-2.906
248	0.960	-3.017
310	0.760	-3.119
372	0.650	-3.251
434	0.440	-3.356
496	0.320	-3.494
558	0.260	-3.585
620	0.180	-3.744
682	0.160	-3.795

Table 3.4

$E_1 = 70 \text{ mV}; E_2 = 90 \text{ mV};$   
 $D_{\text{Cu}} = 4.125 \times 10^{-3} \text{ cm}^2/\text{sec}.$

Time (sec.)	Amps. x $10^{-3}$	log I
0	3.160	-2.500
62	2.200	-2.657
124	1.680	-2.774
186	1.360	-2.866
248	1.060	-2.974
310	0.820	-3.086
372	0.660	-3.180
434	0.560	-3.251
496	0.420	-3.376
558	0.320	-3.494
620	0.240	-3.619

Table 3.9

$E_1 = 70 \text{ mV}; E_2 = 100 \text{ mV};$   
 $D_{\text{Cu}} = 4.189 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. x $10^{-5}$	log I
0	4.590	-2.338
62	3.150	-2.501
124	2.470	-2.607
186	1.950	-2.782
248	1.550	-2.809
310	1.230	-2.910
372	0.950	-3.022
434	0.750	-3.124
496	0.550	-3.259
558	0.430	-3.366
620	0.310	-3.508

Table 3.10

$E_1 = 40 \text{ mV}; E_2 = 10 \text{ mV};$   
 $D_{\text{Cu}} = 4.408 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. x $10^{-5}$	log I
0	4.480	-2.348
62	2.200	-2.657
124	1.720	-2.754
186	1.320	-2.879
248	1.080	-2.966
310	0.840	-3.075
372	0.720	-3.142
434	0.600	-3.221
496	0.520	-3.284

Table 3.11

$E_1 = 90 \text{ mV}; E_2 = 60 \text{ mV};$   
 $D_{\text{Cu}} = 3.75 \times 10^{-3} \text{ cm}^2/\text{sec}.$

Time (sec.)	Amps. x $10^{-3}$	log I
0	5.420	-2.266
62	3.940	-2.404
124	3.140	-2.503
186	2.420	-2.616
248	1.920	-2.703
310	1.620	-2.790
372	1.340	-2.872
434	1.100	-2.958
496	0.940	-3.026
558	0.780	-3.107
620	0.700	-3.154

Table 3.12

$E_1 = 10 \text{ mV}; E_2 = 50 \text{ mV};$   
 $D_{\text{Cu}} = 6.008 \times 10^{-3} \text{ cm}^2/\text{sec}.$

Time (sec.)	Amps. x $10^{-3}$	log I
0	5.040	-2.297
62	2.800	-2.552
124	1.960	-2.707
186	1.400	-2.853
248	1.000	-3.000
310	0.720	-3.939
372	0.520	-3.284
434	0.360	-3.443
496	0.240	-3.619
558	0.120	-9.208

Table 3.13

$$E_1 = 50 \text{ mV}; \quad E_2 = 90 \text{ mV};$$

$$D_{\text{Cu}} = 4.257 \times 10^{-3} \text{ cm}^2/\text{sec}.$$

Time (sec.)	Amps. x $10^{-3}$	log I
0	5.600	-2.251
62	3.800	-2.420
124	2.960	-2.528
186	2.320	-2.634
248	1.840	-2.735
310	1.480	-2.829
372	1.120	-2.950
434	0.880	-3.055
496	0.680	-3.167
558	0.560	-3.251
620	0.440	-3.356
682	0.320	-3.494



CELL NO. 4

Length of  $\text{Cu}_2\text{S}$  = 1.99 cm

Length of  $\text{CuBr}$  = 0.18 cm

Table 4.1

$E_1 = 20 \text{ mV}; E_2 = 30 \text{ mV.}$

$D_{\text{Cu}} = 7.148 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. x $10^{-3}$	log I
0	0.300	-3.520
62	0.145	-3.836
124	0.116	-3.933
186	0.087	-4.059
248	0.067	-4.168
310	0.048	-4.314
372	0.038	-4.411
434	0.029	-4.536
496	0.019	-4.712

Table 4.2

$E_1 = 30 \text{ mV}; E_2 = 40 \text{ mV};$

$D_{\text{Cu}} = 6.470 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. x $10^{-3}$	log I
0	0.640	-3.193
62	0.349	-3.456
124	0.262	-3.581
186	0.203	-3.679
248	0.155	-3.808
310	0.126	-3.896
372	0.097	-4.012
434	0.077	-4.109
496	0.068	-4.167

Table 4.33

$$E_1 = 40 \text{ mV}; \quad E_2 = 60 \text{ mV};$$

$$D_{\text{Cu}} = 6.415 \times 10^{-3} \text{ cm}^2/\text{sec.}$$

Time (sec.)	Amps. x $10^{-3}$	log I
0	1.601	-2.795
62	0.883	-3.053
124	0.660	-3.180
186	0.504	-3.296
248	0.398	-3.001
310	0.310	-3.507
372	0.242	-3.615
434	0.194	-3.712
496	0.155	-3.808
558	0.116	-3.936
620	0.097	

Table 4.4

$$E_1 = 60 \text{ mV}; \quad E_2 = 80 \text{ mV};$$

$$D_{\text{Cu}} = 6.081 \times 10^{-3} \text{ cm}^2/\text{sec.}$$

Time (sec.)	Amps. x $10^{-3}$	log I
0	1.572	-2.803
62	0.951	-3.021
124	0.737	-3.132
186	0.582	-3.234
248	0.466	-3.331
310	0.368	-3.433
372	0.291	-3.535
434	0.233	-3.632
496	0.194	-3.711
558	0.155	-3.808
620	0.116	-3.933

Table 4.5

$$E_1 = 80 \text{ mV}; \quad E_2 = 100 \text{ mV};$$

$$D_{\text{Cu}} = 5.295 \times 10^{-3} \text{ cm}^2/\text{sec.}$$

Time (sec.)	Amps. x $10^{-3}$	log I
0	1.592	-2.798
62	1.068	-2.971
124	0.854	-3.068
186	0.699	-3.155
248	0.563	-3.249
310	0.456	-3.340
372	0.369	-3.433
434	0.301	-3.521
496	0.252	-3.597
558	0.194	-3.711
620	0.155	-3.808

Cell No. 5

Length of  $\text{Cu}_2\text{S} = 2 \text{ cm}$

Length of  $\text{CuBr} = 0.16$

Table 5.1

$E_1 = 10 \text{ mV}; E_2 = 20 \text{ mV}$

$D_{\text{Cu}} = 7.220 \times 10^{-3} \text{ cm}^2/\text{Sec.}$

Time (Sec.)	Amps. x $10^{-3}$	Log I
0	0.883	-3.053
62	0.456	-3.340
124	0.330	-3.481
186	0.242	-3.615
248	0.184	-3.734
310	0.140	-3.851
372	0.111	-3.952
434	0.087	-4.058
496	0.068	-4.167
558	0.053	-4.272

Table 5.2

$E_1 = 20 \text{ mV}; E_2 = 30 \text{ mV};$

$D_{\text{Cu}} = 7.089 \times 10^{-3} \text{ cm}^2/\text{Sec.}$

Time (Sec.)	Amps x $10^{-3}$	log I.
0	0.893	-3.049
62	0.485	-3.313
124	0.359	-3.444
186	0.267	-3.573
248	0.203	-3.690
310	0.150	-3.822
372	0.116	-3.933
434	0.087	-4.058
496	0.068	-4.167
558	0.053	-4.272
620	0.038	-4.411

Table 5.3

$E_1 = 30\text{mV}; E_2 = 40\text{mV};$   
 $D_{\text{Cu}} = 6.963 \times 10^{-3} \text{ cm}^2/\text{Sec.}$

Time (Sec.)	Amps x $10^{-3}$	log I
0	0.878	-3.056
62	0.514	-3.288
124	0.383	-3.416
186	0.291	-3.535
248	0.228	-3.641
310	0.174	-3.757
372	0.131	-3.882
434	0.106	-3.971
496	0.082	-4.083

Table 5.4

$E_1 = 40 \text{ mV}; E_2 = 50\text{mV};$   
 $D_{\text{Cu}} = 6.268 \times 10^{-3} \text{ cm}^2/\text{Sec.}$

Time (Sec.)	Amps x $10^{-3}$	Log I
0	0.917	-3.037
62	0.582	-3.234
124	0.446	-3.350
186	0.349	-3.456
248	0.271	-3.565
310	0.213	-3.670
372	0.169	-3.769
434	0.155	-3.808
496	0.106	-3.971
558	0.087	-4.058
620	0.068	-4.167

Table 5.9

$$E_1 = 50\text{mV}; E_2 = 40\text{mV};$$

$$D_{\text{Cu}} = 6.123 \times 10^{-3} \text{ cm}^2/\text{Sec.}$$

Time (Sec)	Amps. x $10^{-3}$	log I.
0	0.970	-3.012
62	0.631	-0.199
124	0.490	-3.309
186	0.383	-3.416
248	0.305	-3.514
310	0.242	-3.613
372	0.194	-3.711
434	0.160	-3.795
496	0.131	-3.882
558	0.106	-3.971

Table 5.10

$$E_1 = 40\text{mV}; E_2 = 30\text{mV}$$

$$D_{\text{Cu}} = 6.594 \times 10^{-3} \text{ cm}^2/\text{Sec}$$

Time (Sec.)	Amps x $10^{-3}$	log I
0	0.956	-3.019
62	0.592	-3.227
124	0.446	-3.350
186	0.344	-3.462
248	0.271	-3.565
310	0.213	-3.670
372	0.169	-3.769
434	0.140	-3.851
496	0.116	-3.933

$$E_1 = 30\text{mV}; E_2 = 20\text{mV};$$

$$D_{\text{Cu}} = 6.802 \times 10^{-3} \text{ cm}^2/\text{Sec.}$$

Time (Sec.)	Amps x $10^{-3}$	log I
0	0.990	-3.004
62	0.582	-3.234
124	0.436	-3.359
186	0.339	-3.468
248	0.271	-3.565
310	0.218	-3.660
372	0.179	-3.745
434	0.150	-3.822
496	0.126	-3.898
558	0.111	-3.952

$$E_1 = 20\text{mV}; E_2 = 10\text{mV};$$

$$D_{\text{Cu}} = 6.877 \times 10^{-3} \text{ cm}^2/\text{Sec.}$$

Time (Sec.)	Amps. x $10^{-3}$	log I
0	0.961	-3.017
62	0.543	-3.264
124	0.412	-3.384
186	0.325	-3.487
248	0.262	-3.581
310	0.213	-3.670
372	0.179	-3.745
434	0.155	-3.808
496	0.140	-3.851
558	0.131	-3.882
620	0.121	-3.916
682	0.111	-3.952

Table 5.13

$$E_1 = 10\text{mV}; E_2 = 30\text{mV};$$

$$D_{\text{Cu}} = 7.079 \times 10^{-3} \text{ cm}^2/\text{Sec.}$$

Time (Sec.)	Amps. x $10^{-3}$	log I
0	1.776	-2.750
62	0.893	-3.049
124	0.640	-3.193
186	0.485	-3.313
248	0.369	-3.433
310	0.281	-3.550
372	0.213	-3.670
434	0.165	-3.782
496	0.126	-3.898
558	0.097	-4.012

Table 5.14

$$E_1 = 30\text{mV}; E_2 = 50\text{mV};$$

$$D_{\text{Cu}} = 5.70 \times 10^{-3} \text{ cm}^2/\text{Sec.}$$

Time (Sec.)	Amps. x $10^{-3}$	log I
0	1.844	-2.734
62	1.067	-2.971
124	0.796	-3.099
186	0.621	-3.206
248	0.485	-3.313
310	0.378	-3.421
372	0.300	-3.521
434	0.233	-3.632
496	0.194	-3.712
558	0.155	-3.808
620	0.126	-3.898
682	0.097	-4.013



Table 5.15

$$E_1 = 50\text{mV}; E_2 = 70\text{mV};$$

$$D_{\text{Cu}} = 5.157 \times 10^{-3} \text{Cm}^2/\text{Sec}$$

Time (Sec.)	Amps. x $10^{-3}$	log I.
0	1.864	-2.729
62	1.281	-2.892
124	1.009	-2.995
186	0.815	-3.088
248	0.669	-3.174
310	0.543	-3.264
372	0.446	-3.350
434	0.368	-3.433
496	0.310	-3.507
558	0.252	-3.597
620	0.213	-3.670

Table 5.16

$$E_1 = 70\text{mV}; E_2 = 90\text{mV};$$

$$D_{\text{Cu}} = 4.513 \times 10^{-3} \text{Cm}^2/\text{Sec}.$$

Time (Sec.)	Amps. x $10^{-3}$	log I.
0	1.902	-2.720
62	1.417	-2.848
124	1.165	-2.933
186	0.970	-3.012
248.	0.815	-3.088
310	0.679	-3.167
372	0.582	-3.234
434	0.485	-3.313
496	0.417	-3.379
558	0.349	-3.456
620	0.291	-3.535

Table 5.17

$$E_1 = 90\text{mV}; E_2 = 70\text{mV};$$

$$D_{\text{Cu}} = 5.516 \times 10^{-3} \text{Cu}^2/\text{Sec.}$$

Time (Sec.)	Amps. x $10^{-3}$	log I.
0	2.174	-2.662
62	1.679	-2.774
124	1.378	-2.860
186	1.116	-2.952
248	0.912	-3.039
310	0.737	-3.132
372	0.601	-3.220
434	0.485	-3.313
496	0.398	-3.400
558	0.320	-3.494
620	0.252	-3.597

Table 5.18

$$E_1 = 70\text{mV}; E_2 = 50\text{mV};$$

$$D_{\text{Cu}} = 6.146 \times 10^{-3} \text{Cu}^2/\text{Sec.}$$

Time (Sec.)	Amps. x $10^{-3}$	log I.
0	2.038	-2.690
62	1.398	-2.857
124	1.087	-2.963
186	0.873	-3.058
248	0.679	-3.167
310	0.543	-3.264
372	0.427	-3.369
434	0.339	-3.468
496	0.271	-3.565
558	0.213	-3.670
620	0.174	-3.757

Table 5.19

$E_1 = 250\text{mV}$ ;  $E_2 = 30\text{mV}$ ;  
 $D_{\text{Cu}} = 6.146 \times 10^{-3} \text{cm}^2/\text{Sec.}$

Time (Sec.)	Amps. $\times$ $10^{-3}$	log I.
0	1.970	-2.705
62	1.194	-2.923
124	0.893	-3.049
186	0.679	-3.167
248	0.524	-3.280
310	0.407	-3.389
372	0.310	-3.507
434	0.252	-3.597
496	0.194	-3.711
558	0.160	-3.795
620	0.131	-3.882

Table 5.20

$E_1 = 30\text{mV}$ ;  $E_2 = 10\text{mV}$ ;  
 $D_{\text{Cu}} = 6.877 \times 10^{-3} \text{cm}^2/\text{Sec.}$

Time (Sec.)	Amps. $\times$ $10^{-3}$	log I.
0	1.961	-2.707
62	1.058	-2.975
124	0.786	-3.104
186	0.601	-3.220
248	0.465	-3.331
310	0.378	-3.421
372	0.300	-3.521
434	0.262	-3.581
496	0.223	-3.653
558	0.194	-3.712
620	0.174	-3.757
682	0.165	-3.782

Table 5.21

$$E_1 = 10\text{mV}; E_2 = 60\text{mV};$$

$$D_{\text{Cu}} = 6.378 \times 10^{-3} \text{cm}^2/\text{Sec}$$

Time (Sec.)	Amps. x $10^{-3}$	log I.
0	5.840	-2.233
62	3.400	-2.468
124	2.600	-2.585
186	2.000	-2.699
248	1.600	-2.795
310	1.280	-2.892
371	1.000	-3.000
434	0.800	-3.096
496	0.640	-3.193
558	0.520	-3.284

Table 5.22

$$E_1 = 60\text{mV}, E_2 = 110 \text{ mV};$$

$$D_{\text{Cu}} = 4.112 \times 10^{-3} \text{cm}^2/\text{Sec}.$$

Time (Sec.)	Amps. x $10^{-3}$	log I.
0	6.000	-2.218
62	4.560	-2.341
124	3.840	-2.415
186	3.280	-2.484
248	2.800	-2.552
310	2.400	-2.619
372	2.040	-2.690
434	1.760	-2.754
496	1.520	-2.818
558	1.280	-2.892
620	1.120	-2.950
682	0.960	-3.017

Cell No. 6 (Double Cell)

Length of  $\text{Cu}_2\text{S} = 2.02 \text{ Cm}$

Length of  $\text{CuBr} = 0.2 \text{ Cm}$  and  $0.19 \text{ Cm}$

Table 6.1

$E_1 = 10\text{mV}; E_2 = 20\text{mV};$

$D_{\text{Cu}} = 2.740 \times 10^{-3} \text{ Cm}^2/\text{Sec.}$

Time (Sec.)	Amps. x $10^{-3}$	log I.
0	1.165	-2.933
62	0.669	-3.174
124	0.446	-3.350
186	0.291	-3.535
248	0.194	-3.711
310	0.116	-3.933
372	0.068	-4.167
434	0.038	-4.411
496	0.009	-5.013

Table 6.2

$E_1 = 20\text{mV}; E_2 = 30\text{mV};$

$D_{\text{Cu}} = 2.026 \times 10^{-3} \text{ Cm}^2/\text{Sec.}$

Time (Sec.)	Amps. x $10^{-3}$	log I.
0	1.301	-2.521
62	0.815	-3.088
124	0.582	-3.234
186	0.427	-3.369
248	0.310	-3.507
310	0.322	-3.632
372	0.174	-3.757
434	0.126	-3.898
496	0.097	-4.012

Table 6.7

$$E_1 = 70\text{mV}; E_2 = 60\text{mV};$$

$$D_{\text{Cu}} = 1.419 \times 10^{-3} \text{cm}^2/\text{Sec.}$$

Time (Sec.)	Amps. $\times$ $10^{-3}$	$\log I.$
0	1.223	-2.912
62	0.922	-3.035
124	0.757	-3.120
186	0.621	-3.206
248	0.504	-3.296
310	0.407	-3.389
372	0.330	-3.481
434	0.271	-3.565
496	0.218	-3.660
558	0.174	-3.757

Table 6.8

$$E_1 = 60\text{mV}; E_2 = 50 \text{ mV};$$

$$D_{\text{Cu}} = 1.255 \times 10^{-3} \text{cm}^2/\text{Sec.}$$

Time (Sec.)	Amps. $\times$ $10^{-3}$	$\log I$
0	1.320	-2.879
62	0.990	-3.004
124	0.810	-3.091
186	0.669	-3.174
248	0.553	-3.257
310	0.455	-3.340
372	0.378	-3.421
434	0.320	-3.494
496	0.262	-3.581
558	0.223	-3.651
620	0.184	-3.734
682	0.165	-3.782

Table 6.9

$E_1 = 50 \text{ mV}$ ,  $E_2 = 40 \text{ mV}$ ,  
 $D_{\text{Cu}} = 1.496 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. x $10^{-3}$	log I
0	1.339	-2.872
62	0.970	-3.012
124	0.776	-3.109
186	0.621	-3.206
248	0.504	-3.296
310	0.427	-3.369
372	0.349	-3.456
434	0.291	-3.535
496	0.252	-3.597
558	0.213	-3.670

Table 6.10

$E_1 = 40 \text{ mV}$ ,  $E_2 = 30 \text{ mV}$ ,  
 $D_{\text{Cu}} = 1.477 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. x $10^{-3}$	log I
0	1.301	-2.521
62	0.932	-3.030
124	0.737	-3.132
186	0.582	-3.234
248	0.475	-3.322
310	0.388	-3.410
372	0.330	-3.481
434	0.281	-3.550
496	0.242	-3.614
558	0.213	-3.670
620	0.194	-3.711

• Table 6.11

$E_1 = 30 \text{ mV}$ ,  $E_2 = 20 \text{ mV}$ ,  
 $D_{\text{Cu}} = 1.496 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. x $10^{-3}$	log I
0	1.378	-2.863
62	0.951	-3.021
124	0.708	-3.148
186	0.592	-3.227
248	0.475	-3.322
310	0.388	-3.410
372	0.330	-3.481
434	0.291	-3.535
496	0.252	-3.597

Table 6.12

$E_1 = 20 \text{ mV}$ ,  $E_2 = 10 \text{ mV}$ ,  
 $D_{\text{Cu}} = 1.148 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. x $10^{-3}$	log I
0	1.281	-2.892
62	0.786	-3.104
124	0.553	-3.257
186	0.407	-3.389
248	0.233	-3.632
310	0.194	-3.712
372	0.155	-3.808
434	0.135	-3.866



Table 6.13

$E_1 = 10 \text{ mV}$ ,  $E_2 = 30 \text{ mV}$ ,  
 $D_{\text{Cu}} = 2.157 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. x $10^{-3}$	log I
0	2.320	-2.537
62	1.360	-2.866
124	1.080	-2.966
186	0.760	-3.119
248	0.560	-3.251
310	0.400	-3.397
372	0.240	-3.619
434	0.120	-3.920
496	0.040	-4.397

Table 6.14

$E_1 = 20 \text{ mV}$ ,  $E_2 = 40 \text{ mV}$ ,  
 $D_{\text{Cu}} = 2.633 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. x $10^{-3}$	log I
0	2.40	-2.619
62	1.60	-2.795
124	1.120	-2.950
186	0.800	-3.096
248	0.560	-3.251
310	0.360	-3.443
372	0.240	-3.619
434	0.160	-3.795

Table 6.15

$E_1 = 30 \text{ mV}$ ,  $E_2 = 50 \text{ mV}$ ,  
 $D_{\text{Cu}} = 1.602 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. $\times$ $10^{-3}$	log I
0	2.480	-2.605
62	1.840	-2.735
124	1.400	-2.853
186	1.120	-2.950
248	0.880	-3.055
310	0.680	-3.167
372	0.560	-3.251
434	0.480	-3.318
496	0.400	-3.397
558	0.320	-3.494

Table 6.16

$E_1 = 50 \text{ mV}$ ,  $E_2 = 70 \text{ mV}$ ,  
 $D_{\text{Cu}} = 1.323 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. $\times$ $10^{-3}$	log I
0	2.000	-2.522
62	2.280	-2.642
124	1.840	-2.735
186	1.520	-2.818
248	1.240	-2.906
310	1.040	-2.983
372	0.920	-
434	0.760	-3.119
496	0.640	-3.193
558	0.560	-3.251
620	0.480	-3.318
682	0.400	-3.397

Table 6.17

$E_1 = 60 \text{ mV}$ ,  $E_2 = 80 \text{ mV}$ ,  
 $D_{\text{Cu}} = 1.381 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. $\times$ $10^{-3}$	log I
0	2.400	-2.619
62	1.860	-2.744
124	1.480	-2.829
186	1.200	-2.920
248	0.960	-3.096
310	0.800	-3.193
372	0.640	-3.284
434	0.520	-3.397
496	0.400	-3.494
558	0.320	-3.619

Table 6.18

$E_1 = 70 \text{ mV}$ ,  $E_2 = 90 \text{ mV}$ ,  
 $D_{\text{Cu}} = 1.003 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. $\times$ $10^{-3}$	log I
0	3.040	-2.517
62	2.440	-2.612
124	2.040	-2.690
186	1.760	-2.754
248	1.480	-2.829
310	1.280	-2.892
372	1.120	-2.950
434	0.960	-3.017
496	0.840	-3.075
558	0.720	-3.142
620	0.640	-3.193

Table 6.19

$E_1 = 80 \text{ mV}$ ,  $E_2 = 100 \text{ mV}$ ,  
 $D_{\text{Cu}} = 1.091 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. $\times 10^{-3}$	$\log I$
0	2.720	-2.566
62	2.320	-2.634
124	1.920	-2.716
186	1.640	-2.785
248	1.440	-2.841
310	1.240	-2.950
372	1.080	-2.974
434	0.920	-3.036
496	0.840	-3.075
558	0.720	-3.142

Table 6.20

$E_1 = 10 \text{ mV}$ ,  $E_2 = 40 \text{ mV}$ ,  
 $D_{\text{Cu}} = 1.841 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. $\times 10^{-3}$	$\log I$
0	3.600	-2.443
62	2.000	-2.699
124	1.720	-2.764
186	1.280	-2.892
248	0.960	-3.017
310	0.720	-3.142
372	0.520	-3.284
434	0.400	-3.397
496	0.320	-3.494
558	0.240	-3.619
620	0.160	-3.795

Table 6.21

$E_1 = 40 \text{ mV}$ ,  $E_2 = 70 \text{ mV}$ ,  
 $D_{\text{Cu}} = 1.475 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. x $10^{-3}$	log I
0	4.000	-2.397
62	2.880	-2.540
124	2.240	-2.649
186	1.760	-2.754
248	1.400	-2.853
310	1.120	-2.950
372	0.880	-3.055
434	0.720	-3.142
496	0.600	-3.221
558	0.480	-3.318

Table 6.22

$E_1 = 70 \text{ mV}$ ,  $E_2 = 40 \text{ mV}$ ,  
 $D_{\text{Cu}} = 1.406 \times 10^{-3} \text{ cm}^2/\text{sec.}$

Time (sec.)	Amps. x $10^{-3}$	log I
0	4.480	-2.348
62	3.560	-2.448
124	2.880	-2.540
186	2.320	-2.634
248	1.880	-2.725
310	1.520	-2.818
372	1.240	-2.906
434	1.040	-2.983
496	0.840	-3.075
558	0.720	-3.142
620	0.600	-3.221

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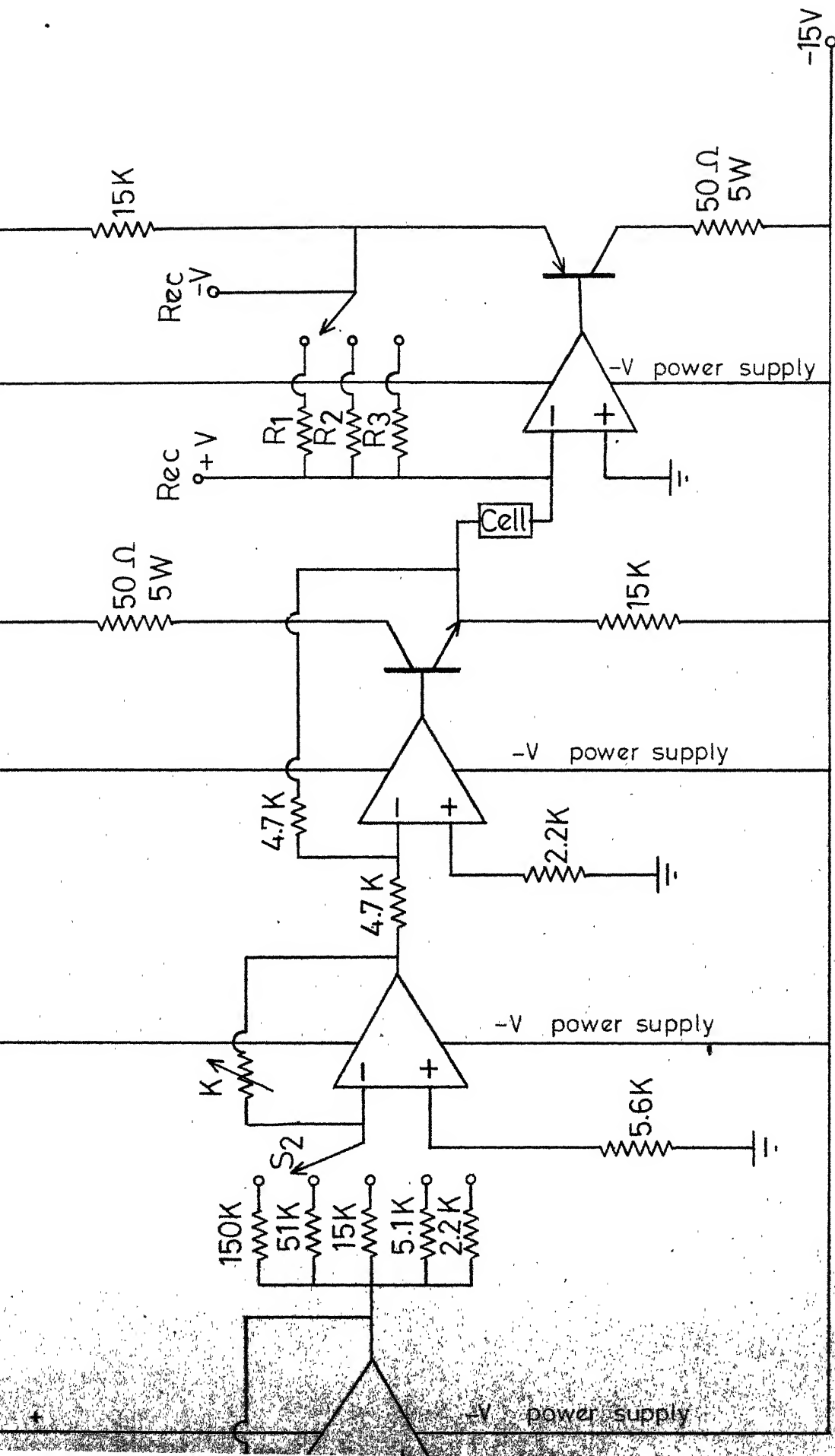
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Detailed electrical circuit of the regulated power supply

FIG.4



Figure 7 and table 4 show the variation of chemical diffusivity with activity for a cell with 2 cm long  $\text{Cu}_2\text{S}$  electrode. It is interesting to note that the diffusion coefficient decreases when copper activity in cuprous sulfide decreases. This kind of behaviour was reported for some of the oxide systems discussed in Chapter 2.

Table 4

Variation of Chemical Diffusivity with activity  
of Copper in Cuprous Sulfide.

Length of  $\text{Cu}_2\text{S}$  = 2.0 cm. Length of  $\text{CuBr}$  = 0.16 cm.

$E_{\text{cell}}$ mV	$a_{\text{Cu}}$	$\bar{D}_{\text{Cu}}$ $\text{cm}^2/\text{sec.}$
15	0.7722	$7.22 \times 10^{-3}$
20	0.7087	$7.079 \times 10^{-3}$
25	0.6502	$7.039 \times 10^{-3}$
35	0.5470	$6.953 \times 10^{-3}$
45	0.4604	$6.268 \times 10^{-3}$
55	0.3876	$6.123 \times 10^{-3}$
65	0.3259	$5.676 \times 10^{-3}$
80	0.2519	$4.513 \times 10^{-3}$
85	0.2311	$4.112 \times 10^{-3}$

independent of time. This behaviour is true even for higher currents as against anodic behaviour. This is probably because void formation is absent in this case and always a good electrode/electrolyte interfacial contact is maintained.

The polarisation experiments indicate that it would be better to use the Cu/CuBr interface as a cathode in the diffusivity measurements. This is the case in the "pumpout" experiments where copper is removed from cuprous sulfide during the diffusion process. Some influence of polarisation would be expected when using copper as the anode as in the "pumpin" experiments. The effect, however, would be small as there is no significant polarisation. The diffusivity values from the "pumpout" curves were found to be somewhat larger than those calculated from the

Table 5

$D_{\text{Cu}}$ (self) Wagner <sup>5</sup>	$\delta$	$a_{\text{Cu}}$	$\frac{d \ln a_{\text{Cu}}}{d \ln C_{\text{Cu}}}$	$\bar{D}_{\text{Cu}}$ (Experimental)	$D_{\text{Cu}}$ (self) calculated
$9 \times 10^{-6}^*$	0.0020	0.23	690	$4.112 \times 10^{-3}$	$5.960 \times 10^{-6}$
	0.0018	0.25	862.4	$4.513 \times 10^{-3}$	$5.234 \times 10^{-6}$
	0.0012	0.36	1035	$5.513 \times 10^{-3}$	$5.378 \times 10^{-6}$

\*  $D_{\text{Cu}}$  (self) was calculated from conductivity Data.

Table 1.9

$E_1 = 100 \text{ mV}; E_2 = 70 \text{ mV};$   
 $D_{\text{Cu}} = 0.853 \times 10^{-3} \text{ cm}^2/\text{sec}.$

Time (Sec.)	Amps. x $10^{-3}$	log I
0	4.420	-2.354
62	2.620	-2.581
124	1.740	-2.759
186	1.340	-2.872
248	1.140	-2.943
310	1.020	-2.991
372	0.860	-3.065
434	0.780	-3.107
496	0.700	-3.154

Table 1.10

$E_1 = 10 \text{ mV}; E_2 = 50 \text{ mV};$   
 $D_{\text{Cu}} = 2.321 \times 10^{-3} \text{ cm}^2/\text{sec}.$

Time (sec.)	Amps. x $10^{-3}$	log I
0	3.220	-2.492
62	1.460	-2.835
124	0.900	-3.045
186	0.580	-3.236
248	0.380	-3.420
310	0.300	-3.522
372	0.220	-3.657
434	0.180	-3.744
496	0.120	-3.920
558	0.100	-4.000
620	0.080	-4.096

Table 3.7

$E_1 = 10 \text{ mV}; E_2 = 40 \text{ mV};$   
 $D_{\text{Cu}} = 6.010 \times 10^{-3} \text{ cm}^2/\text{sec}.$

Time (sec.)	Amps. x $10^{-3}$	log I
0	3.560	-2.448
62	1.768	-2.752
124	1.256	-2.901
186	0.880	-3.055
248	0.632	-3.199
310	0.440	-3.356
372	0.384	-3.415
434	0.200	-3.699
496	0.120	-3.920
558	0.080	-4.096
620	0.016	-4.795

Table 3.8

$E_1 = 40 \text{ mV}; E_2 = 70 \text{ mV};$   
 $D_{\text{Cu}} = 4.808 \times 10^{-3} \text{ cm}^2/\text{sec}.$

Time (sec.)	Amps. x $10^{-3}$	log I
0	4.240	-2.372
62	2.320	-2.634
124	1.680	-2.774
186	1.240	-2.906
248	0.920	-3.036
310	0.720	-3.142
372	0.560	-3.251
434	0.440	-3.356
496	0.320	-3.494
558	0.240	-3.619
620	0.160	-3.795
682	0.120	-3.920

Table 5.7

$E_1 = 70\text{mV}; E_2 = 60\text{mV};$   
 $D_{\text{Cu}} = 5.476 \times 10^{-3} \text{cm}^2/\text{Sec.}$

Time (Sec.)	Amps x $10^{-3}$	log I
0	1.019	-2.992
62	0.747	-3.126
124	0.597	-3.223
186	0.480	-3.318
248	0.388	-3.410
310	0.310	-3.507
372	0.252	-3.597
434	0.203	-3.690
496	0.160	-3.795
558	0.126	-3.898

Table 5.8

$E_1 = 60\text{mV}; E_2 = 50\text{mV};$   
 $D_{\text{Cu}} = 6.023 \times 10^{-3} \text{cm}^2/\text{Sec.}$

Time (Sec.)	Amps x $10^{-3}$	log I
0	1.009	-2.995
62	0.699	-3.155
124	0.548	-3.260
186	0.432	-3.364
248	0.339	-3.468
310	0.271	-3.565
372	0.213	-3.670
434	0.174	-3.757
496	0.135	-3.866
558	0.106	-3.971
620	0.087	-4.058
682	0.077	-4.109

Table 6.5

$$E_1 = 50\text{mV}; E_2 = 60\text{mV};$$

$$D_{\text{Cu}} = 1.343 \times 10^{-3}$$

Time (Sec.)	Amps. $\times$ $10^{-3}$	log I.
0	1.184	-2.926
62	0.864	-3.063
124	0.699	-3.155
186	0.563	-3.249
248	0.456	-3.340
310	0.378	-3.421
372	0.310	-3.507
434	0.252	-3.597
476	0.213	-3.670
558	0.174	-3.757

Table 6.6

$$E_1 = 60\text{mV}; E_2 = 70\text{mV};$$

$$D_{\text{Cu}} = 1.180 \times 10^{-3} \text{ cm}^2/\text{Sec.}$$

Time (Sec.)	Amps. $\times$ $10^{-3}$	log I.
0	1.184	-2.926
62	0.893	-3.049
124	0.737	-3.132
186	0.616	-3.210
248	0.514	-3.288
310	0.432	-3.364
372	0.369	-3.433
434	0.310	-3.507
496	0.262	-3.581
558	0.223	-3.651
620	0.184	-3.734
682	0.155	-3.808